

2 Methodology and the Model Alloys

2.1 Structural Particularities of Fe-based BMGs

In a BMG the atoms are randomly distributed. Despite that, many BMGs show a kind of a particular short-range order. In most of the cases such order enhances the stability of a glass, as for example the group of Pd-based glasses [Ino00]. The Fe-based BMGs of the type LTM-ETM-Metalloid (as, for example, FeCo-Nb-SiB) behave also in a particular way. Inoue et al. showed that the presence of the ETM (i.e. Nb) up to 4–6 at.% may enhance the GFA by stabilizing the SLR [Ino04]. In fact, starting from Fe₈₀B₂₀ and adding Nb, a new behavior was discovered. The stable (equilibrium) crystalline phases which are expected to appear upon devitrification of such glasses are α -Fe and Fe₂B. The presence of Nb changes the succession of crystallization. The first phase which form upon heating from the glassy state is a complex one, of the type Fe₂₃B₆. It is a metastable phase which further will transform in the equilibrium products, but at a much higher temperature. This phase is basically fcc-like and has a large lattice parameter of about 1.2 nm, including 96 atoms in its volume unit. Its formation requires a high energy, as well as long diffusion path, and this explain why the amorphous precursors show such good thermal stability and relatively high GFA. Structural, the glass itself develops a kind of short range order, a unique network-like structure in which trigonal prisms consisting of Fe and B atoms are connected with each other in an edge- and plane-shared configuration modes through glue atoms of Nb [Ima01, Ino04]. Furthermore, Poon et al. [Poo03] have pointed out that the large (L) and small (S) atoms may form a strong L–S percolating network or reinforced ‘backbone’ in the amorphous structure, and presumably, this backbone structure can enhance the stability of the undercooled melt, which further suppresses crystallization. In fact, the local triangular unit is quite similar to Fe₃B crystal, as demonstrated by Matsubara et al. [Mat01].

Let’s discuss the above statements in more details. In the Fe₃B crystal, the triangular prisms are connected in two different ways as it is schematically shown in Fig. 2.1. One third of Fe atoms are connected by sharing Fe at the vertex of the prism and the others by sharing the edge. The Nb elements occupy the vertices in a random manner, and not only Nb can be used but also other large ETM elements like Zr or Cr. J. Poon [Poo03] took in account the percentage and the radius of the atoms which are present in the BMG (atom size-composition relationship). The LTM-ETM-Metalloid glasses contains midsize atoms as the majority

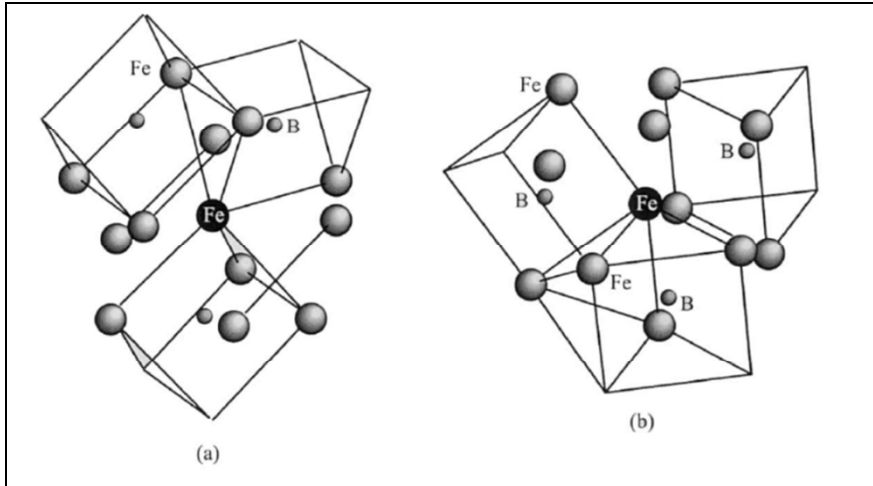


Fig. 2.1: Schematic diagrams of atomic arrangements (a) for the vertex-sharing and (b) edge-sharing triangular prisms in the Fe_3B crystal. Only atoms in the near neighbor region around Fe at the center (solid circle) are drawn. Reprinted from *Materials Science and Engineering A*, vol. 312, E. Matsubara, S. Sato, M. Imafuku, T. Nakamura, H. Koshiba, A. Inoue, Y. Waseda, *Structural Study of Amorphous $\text{Fe}_{70}\text{M}_{10}\text{B}_{20}$ ($\text{M}=\text{Zr}, \text{Nb}$ and Cr) Alloys by X-ray Diffraction*, pages 136-144, Copyright 2001, with permission from Elsevier

component (Fe and/or Co, content slightly above 70 at.%), small atoms (the metalloids) as the next-majority component (around 20 at.%), and large-size atoms as the minority component (as for example Nb, content less than 10 at.%), labelled as the “majority atom–small atom–large atom” (MSL) class. In these alloys the heat of mixing is negative. Presumably, the backbone structure can enhance the stability of the undercooled melt, which further suppresses crystallization, in addition to other favorable glass-forming factors that are present in these compositions. However, if the concentration of the L atoms is significantly higher than 10 at.%, there will be an increasing tendency for the L atoms to cluster, which will effectively reduce the interaction between the L atoms and the M and S atoms. Thus, the optimal content of large atoms for forming BMGs of the MSL type appears to be near 10 at.%. The percentage of S atoms is around 20 at.%, while the L atoms are less than 10 at.%. Thus, the L and S atoms may be seen as forming a strong L–S percolating network or reinforced “backbone” in the amorphous structure, as illustrated in Fig. 2.2.

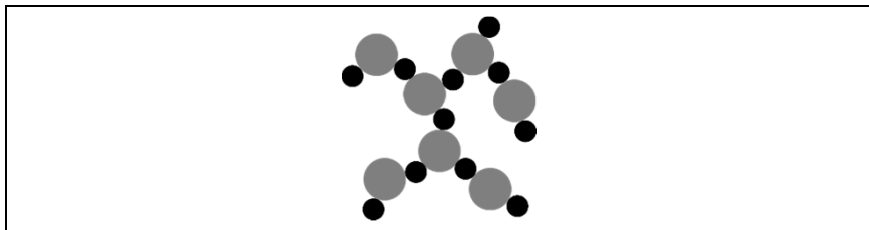


Fig. 2.2: Sketch of atomistic network/ backbone formed by the large atoms and small atoms in the MSL class metallic glasses (upon [Poo03])

The data published so far prove this theory [Sur11], but the presence of 10 at.% of a large nonmagnetic atoms may deteriorate the ferromagnetic properties. If we consider FeCoBSiNb as a model BMG, our findings, corroborated with other experimental results presented in literature, indicates that a good compromise between GFA and soft magnetic properties is obtained when the Nb content is 4 at.%.

Upon crystallization, such kind of glasses form the metastable Fe_{23}B_6 type phase. In this structure, the cubo-octahedra and the cubes formed by metal atoms are connected with metalloid atoms. Thus, the metalloid atoms are surrounded by 8 metal atoms to form an Archimedean square antiprism. These antiprisms ought to be symmetrically arranged in the Fe_{23}B_6 structure. In the amorphous Fe-B alloys containing a bit more than 20 at.% B, the local atomic structure is characterized by the non-periodic network of trigonal prisms. The coordination number around the metalloid atoms is expected to be 6 with the first nearest neighbours. Therefore, the change in the chemical short-range order from the trigonal prism to the Archimedean square antiprism as well as simultaneous arrangement of these polyhedra to form Fe_{23}B_6 type symmetry should occur for the phase transformation from the amorphous phase to the primary crystalline phase. A drawing of such phase is presented in Fig. 2.3.

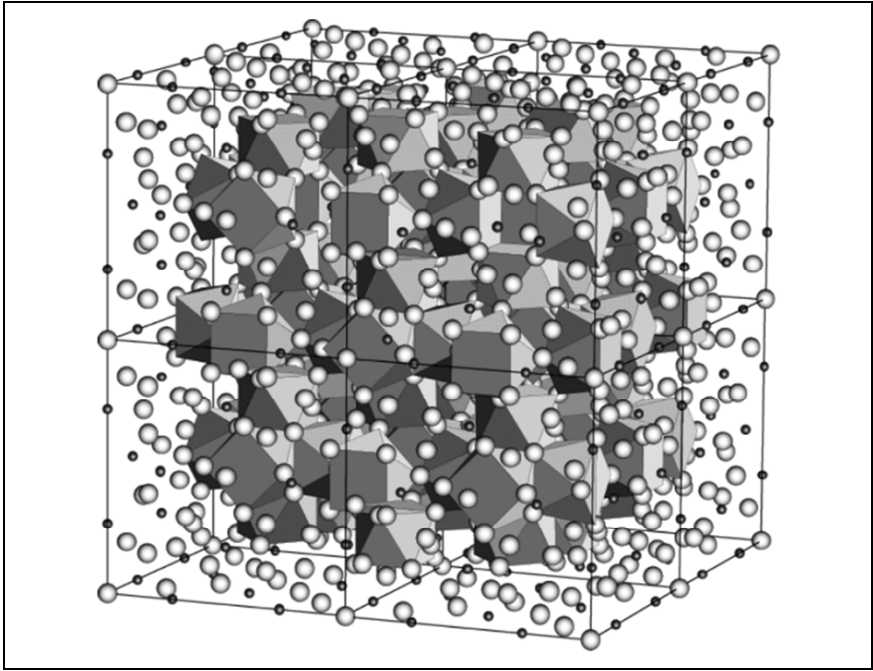


Fig. 2.3: Sketch showing the Fe_{23}B_6 -type metastable phase. Reprinted from Materials Transactions, vol. 43, no. 8, Takahiro Nakamura, Hisato Koshiba, Muneyuki Imafuku, Akihisa Inoue and Eiichiro Matsubara, Determination of Atomic Sites of Nb Dissolved in Metastable Fe_{23}B_6 Phase, pages 1918-1920, Copyright 2002, with permission from The Japan Institute of Metals and Materials

2.2 Strategy for Assessing the Glassy Nature of the Samples

2.2.1 Theoretical Aspects

To study the variation of the GFA one has to decide which parameters should be considered. Taking in account the requirements for industrial applications, it is reasonable to consider the geometry of the samples as a measure of the GFA. In extenso, if we stick to a specific simple geometry like full cylinders (rods) of a certain length, the maximum achievable diameter for which the products are still amorphous is an indication of the GFA. In other words, the alloy which assures the preparation of a fully amorphous rod in 3 mm diameter (for example) has a better GFA than one which can be amorphised only as rod with 2 mm diameter

(assuming that the length is the same). The amorphous nature of the samples must be investigated by corroborating several measurement techniques. In the following are briefly described the means used in the present study (the experimental procedures are given in extenso in Chapter 3).

X-ray diffraction (XRD). The presence of crystals in the amorphous matrix can be determined by performing X-ray diffraction studies. The well-used Bragg-Brentano configuration may have some limitations: it is difficult to rule-out the presence of a small volume fraction of crystalline inclusions or crystalline nuclei. A better solution is the transmission configuration, but for laboratory devices that use characteristic X-ray tubes there it is a severe restraint regarding the sample thickness (i.e. to approx. 100 μm and below). A far better and reliable solution is to use the synchrotron hard X-ray- its brilliance is high enough to pass through a mm-thick sample and its higher energy (i.e. lower wave length) as compared with the X-ray tubes assures a much better resolution when it is about to detect the nano-features embedded in the amorphous matrix. The width and the intensity of the main halo bring as well important details about the amorphicity degree: a more disorganized structure is characterized by a wider diffraction peak with lower intensity.

Differential scanning calorimetry (DSC). The presence of main events that distinguish the glassy structure, as the glass transition and crystallization events, as well as the extension of the SLR, can be easily put in evidence upon DSC measurements. Additionally, the crystallization enthalpy ΔH_x is a good measure of the amorphicity degree (higher the enthalpy, lower the crystalline fraction) and it scales linearly with the crystalline fraction through the following equation:

$$f_x = \frac{\Delta H_{\text{amorph}} - \Delta H_{\text{actual}}}{\Delta H_{\text{amorph}}} \quad (2.1)$$

where f_x is the crystalline fraction, ΔH_{amorph} the crystallization enthalpy of a fully amorphous sample and ΔH_{actual} the crystallization enthalpy of the actual investigated samples.

Time-resolved X-ray diffraction in transmission configuration. This is a very effective method to study the relaxation and crystallization behavior, and therefore to assess the stability of the glassy phase. Such kind of measurements are done in transmission configuration, using the high-energy high intensity monochromatic synchrotron beam.

Magnetic measurements, in particular the coercivity H_c . This method can be successfully applied to magnetic BMGs. Because of the absence of crystalline

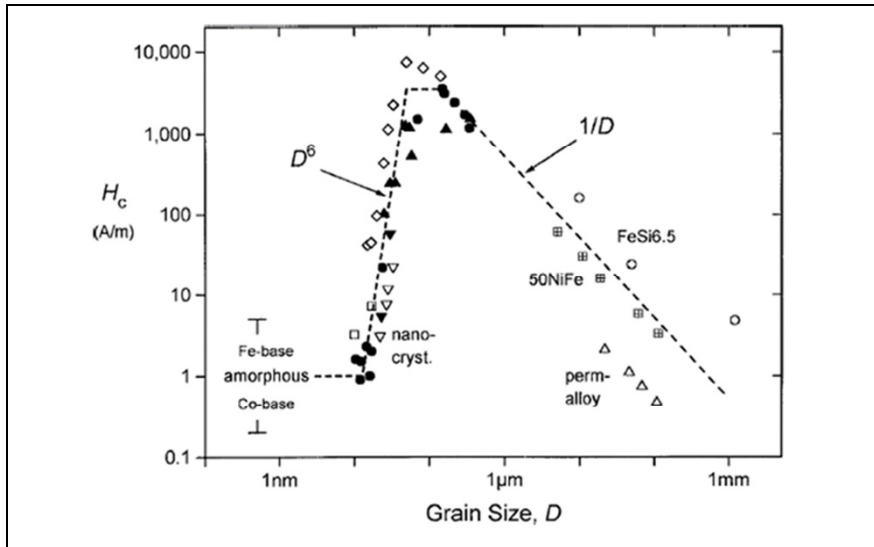


Fig. 2.4: Coercivity H_c vs. grain size D for various soft magnetic metallic alloys: Fe-Nb-Si-B (solid up triangles), Fe-Cu-Nb-Si-B (solid circles), Fe-Cu-V-Si-B (solid and open down triangles), Fe-Zr-B (open squares), Fe-Co-Zr (open diamonds), NiFe alloys (+ center squares and open up triangles) and Fe-6.5Si (open circles). Reprinted from K.H.J. Buschow (ed.) Handbook of Magnetic Materials, vol. 10, Giselher Herzer, Chapter 3: Nanocrystalline Soft Magnetic Alloys, pages 415-462, Copyright 1997, with permission from Elsevier

anisotropy, the ferromagnetic BMGs exhibit good soft magnetic properties, characterized by extremely low coercivity and high permeability. Nevertheless, residual anisotropies may be present, such as shape anisotropy or stress-induced anisotropy, caused by internal mechanical stress induced during the preparation procedure. The unwanted anisotropies can be reduced by annealing the samples at elevated temperatures, but below T_g . This method of investigation can prove the presence of some crystals even when they are not detected by the X-ray diffraction studies and therefore can be considered as the most sensitive one for our samples. Its reliability resides in the fact that for very small crystalline particles, the coercivity scales with the sixth power of their geometrical dimensions. The variation of the coercivity for nanocrystalline magnetic materials was in details summarized by G. Herzer in [Her97], from where Fig. 2.4 is taken. From there it is clear that a fully amorphous sample should have the coercivity below 10 A/m.

Additionally, when there are still doubts regarding the amorphous nature of the samples, high resolution transmission electron microscopy (HR-TEM) can be

involved. But there are again disadvantages, due to the fact that (a) the probes for TEM are very small and by chance they may not show any crystals if the crystals are not random distributed in the sample, and (b) during the TEM probe preparation process the sample might (nano)crystallize and the TEM image will be affected by artefacts.

2.2.2 *Technical Aspects*

It was mentioned that there does not exist a strict general recipe to find compositions able to form BMGs. Consequently, the minor addition of elements different from the main constituents may affect in a different manner the GFA of different composition, even within the same class of alloys. However, first of all composition with relatively high GFA must be identified. This is why a large amount of work was conducted in this direction and an extensive literature survey was performed.

Generally, the impurities can be regarded as small addition even when the concentration is relatively low. As an example, in the case of Finemet® alloy (Fe-CuNbSiB), there the Cu content is just 1 at.%, but its presence changes completely the behavior of the glass. Now there it is the question if Cu can be regarded anymore as an “impurity” or up to which content one speaks about “impurities”. For example, and as it will be shown later, a similar thing happens with one of our investigated alloys. There the Nb content is maximum 4 at.%, so the presence of other elements even at 1 at.% or less should be treated as an addition. This came because the used raw materials at the laboratory scale usually have a purity superior to 99 %- the BMGs are very sensitive to the cleanliness of the elements. Due to this fact, the first attempts to establish the role of the impurities on the GFA must start directly from the used materials. As will be presented in the next chapters, for each investigated composition several master alloys were prepared, using only pure elements, using mixture of pure elements and industrial pre-alloys, using only industrial pre-alloys, using pre-alloys made in-house from pure elements etc. The things become more complicated when a new alloy class (or a new composition) is investigated. Usually, there one starts from the premises that the highest GFA is obtained when the purest elements are used. After that, one can substitute some elements partially or totally with “dirty” pre-alloys etc. This gradual way of investigating the alloys has several good parts. All used materials, excepting the pure elements, were chemically analyzed at IFW in order to find-out the actual composition. Studying the changes in the GFA produced by the use of different constituents one can establish the global role of some impurities on the GFA. The other good aspect which results from this method of investigation is the possibility to find which alloy and up to which dimensions can be prepared by using industrial available raw materials.

Other way to investigate the role of the impurities is to take an alloy with known GFA and mix it deliberately with small quantities of different other elements. This is a good method but very laborious, which needs high allocation of manpower and financial resources. A way to simplify the work is to study the crystallization behavior. Once the first crystallized product(s) is/are found, one has to assess which elements may trigger the formation of that specific phase(s). Now, small addition of those elements may be done onto the master alloy. In this way it is possible to find out up to which level several separate additions may affect the GFA.

A third way to investigate the role of the impurities, perfectly suitable for finding especially the effect of Oxygen, is to cast the alloys under controlled atmosphere, at different partial pressure of the air. After, the Oxygen level in each sample should be measured and the results analyzed together with the observed GFA.

2.3 The Selection of the Investigated Alloys

The motivation of the entire work stays under the possibility to cast BMGs with soft magnetic properties using industrial raw elements and pre-alloys. Obviously, there are several classes of alloys worth to be investigated. However, in order to study the alloy optimization, focused on finding and understanding the influences of the impurities on the glass forming ability, one should start from a known alloy with good castability, high GFA and good soft magnetic properties. We tried to identify some of such alloys using information available in the scientific literature. What should be mentioned here is that the achievements mentioned in scientific literature depend on the working environment and technology used, as well as on the purity or condition of the used raw materials. Also, the available literature data are obtained at a laboratory scale. In many cases, the reproducibility of the results is quite poor and the results presented in a paper do not necessarily reflect the behavior of the entire set of samples.

2.3.1 Literature Alloy (Fe,Co)-Nb-(B,Si)

Taking in account the available data published so far, the best ferromagnetic alloy system, which is able to retain the amorphous structure when cast as samples with relatively large dimensions, is (Fe,Ni,Co)-Nb-(B,Si). It has the starting point from Fe₇₅B₁₅Si₁₀ alloy, which can be cast by melt spinning as ribbons with a maximum achievable thickness of 250 μm [Hag81]. The first attempts to cast a BMG from a similar composition were in 2002 with FeBSiNb [Ino02]. The Nb

Table 2.1: FeBSiNb compositions investigated by Inoue *et al.* [Ino02].

Alloy	Maximum sample thickness	Thermal stability			Soft magnetic properties		
	t_{max} [mm]	T_g [K]	ΔT_x [K]	T_g/T_l	T_C [K]	B_s [T]	H_c [A/m]
$(Fe_{0.75}B_{0.15}Si_{0.10})_{99}Nb_1$	0.5	815	43	0.56	684	1.50	3.7
$(Fe_{0.75}B_{0.15}Si_{0.10})_{98}Nb_2$	1	812	58	0.57	650	1.49	3.5
$(Fe_{0.75}B_{0.15}Si_{0.10})_{96}Nb_4$	1.5	835	50	0.61	593	1.47	2.9
$(Fe_{0.775}B_{0.125}Si_{0.10})_{98}Nb_2$	0.5	760	N/A	0.54	634	1.51	3.7

addition is the reason of a significantly increase of GFA, as it was discussed in the previous paragraph. Due to the fact that Nb content is low and it is present in the master alloy at the expenses of all other elements, in the writing of the compositions the Nb is placed at the end. Table 2.1 show a short summary of these compositions [Ino02]. As it can be seen, the best GFA is attained when Nb content is 4 at.% and the soft magnetic properties, i.e. Curie temperature T_C , magnetic flux density at saturation B_s and coercivity H_c , are very good.

Further, the composition was developed and in 2006 was reported first 2 mm diameter rod from $(Fe_{75}B_{20}Si_5)_{96}Nb_4$ alloy [Ino06]. Several investigations conducted over time and focused on the increase of GFA established that Fe can be substituted partial or total by Co or Ni (or both of them), but the price was the deterioration of soft magnetic properties, especially decreasing of saturation magnetization. The works concluded that the partial replacement of Fe by Co or Co+Ni causes a significant increase in the glass-forming ability through the decrease in melting and liquidus temperatures, leading to the formation of bulk glassy alloys with diameters up to at least 5 mm for $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ [Ino06, She07]. A summary of the thermal stability and, implicitly, the GFA, in the case of Fe-Co-Ni alloys is presented in Table 2.2. The maximum achievable diameter is 5 mm in the case of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$.

From the presented data is clear that the best glass former is $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$. Further, using special techniques including melting together with a fluxing agent (dehydrated B_2O_3 in this case), Inoue's group succeeded to cast this composition up to a diameter of 7.7 mm, concluding that

Table 2.2: Maximum critical diameter, thermal stability and mechanical properties for the Fe-Co-Ni-B-Si-Nb glassy alloys.

Alloy	Maximum sample thickness	Thermal stability		
	t_{max} [mm]	T_g [K]	ΔT_x [K]	T_g/T_l
$[(Fe_{0.9}Co_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2	832	45	0.570
$[(Fe_{0.8}Co_{0.2})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2.5	830	50	0.580
$[(Fe_{0.7}Co_{0.3})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	3.5	828	50	0.586
$[(Fe_{0.6}Co_{0.4})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4	825	50	0.586
$[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	5	820	50	0.587
$[(Fe_{0.8}Co_{0.1}Ni_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	2.5	818	55	0.606
$[(Fe_{0.6}Co_{0.1}Ni_{0.3})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	3	792	60	0.608
$[(Fe_{0.6}Co_{0.2}Ni_{0.2})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4	800	65	0.611
$[(Fe_{0.6}Co_{0.3}Ni_{0.1})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$	4	813	65	0.613

“this bulk specimen is the thickest of any soft magnetic glassy alloys formed until now” [Bit06]. The used procedure in order to produce this BMG was:

1. Preparation of an eutectic FeNb pre-alloy 75Nb 25Fe (wt.%) by arc melting of pure Nb 99.9% and Fe 99.99%.
2. Arc melting together of Fe 99.9 % and Co 99.9% metals lumps, B 99.5% and Si 99.999% crystals and the Nb–Fe prealloy.
3. The B_2O_3 99.999%, (nominally anhydrous) was preheated at 1273 K (1000 °C) for 130 ks (*sic!*, i.e. ~36 h) sealed in a quartz crucible under vacuum better than 1 Pa ($\sim 10^{-2}$ mbar).
4. Small parts of the previous prepared mast alloy together with the annealed B_2O_3 was sealed in a quartz tube 7.7 mm thick (internal diameter), the volumetric flux-to-alloy ratio being 50-70% vol. The mixture was melted under Ar flow by a torch, held at temperatures well in excess of the liquidus temperature for 100–200 s (~2-3 min), and then cooled to a temperature where B_2O_3 was still molten. This thermal cycle was repeated several times (3-5 times) and at the end the tube was quenched (dropped) in water. The resulted samples are presented in Fig. 2.5 left side ([Bit06]).

In Fig. 2.5, left side, one can observe that the BMGs have very short lengths, and the geometry of the 7.7 mm diameter rod is close to a sphere, having a length of

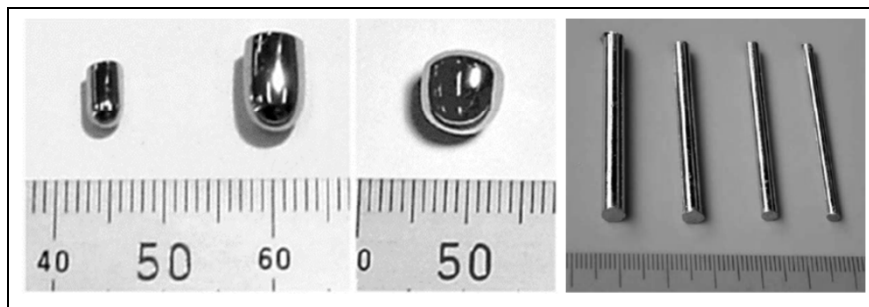


Fig. 2.5: Left side: the $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ fluxed BMGs. Reprinted from Applied Physics Letters, vol. 88, T. Bitoh, A. Makino, A. Inoue, A. L. Greer, Large Bulk Soft Magnetic $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ Glassy Alloy Prepared by B_2O_3 Flux Melting and Water Quenching, article 182510, Copyright 2006, with the permission of AIP Publishing. Right side: several not-fluxed $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ BMGs with diameters up to 5 mm. Reprinted from Intermetallics, vol. 14, A. Inoue, B.L. Shen, C.T. Chang, Fe- and Co-based Bulk Glassy Alloys with Ultrahigh Strength of Over 4000 MPa, pages 936-944, Copyright 2006, with permission from Elsevier

only ~ 7 mm. However, previous reports coming from the same group have shown BMGs with cylindrical shape, obtained by direct casting of an-fluxed master alloy, having maximum 5 mm diameter and a length of 5 cm (see Fig. 2.5, right side).

It must be mentioned here that all results which reports a maximum achievable diameter of 5 mm and a length of 5 cm for $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ BMG comes from the same group, i.e. Inoue's group in Sendai, Japan. Other available papers or results presented during some International meetings or Conferences mentioned that for a length of 5 cm only a maximum 2-3 mm diameter can be attained (dimensions for which the samples are still fully amorphous). In our lab the maximum achievable diameter (in the case of this composition, without fluxing the master alloy) is 3 mm for a length of 5 cm. Interesting is that fully amorphous samples with 2 mm diameter and 5 cm in length can be relatively easy to produce, even from master alloys which uses industrial raw elements/pre-alloys. As mentioned earlier, the purity of the starting raw materials, the casting technique used, the casting parameters, as well as the experience of the operator play a very important role in the fabrication of these BMGs. In the current work, the master alloy with the nominal composition $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ is the first one chosen for the comprehensive study of what influences its GFA.

2.3.2 Literature Alloy Fe-Mo-(P,C,B,Si)

It is known that an industrial pre-alloy or pig iron contains more than only traces of C. This is why, in order to assess the GFA of a BMG made using industrial raw materials, a composition with C is necessary. Combining the achievements presented in literature, together with our own expertise, another possible alloy, also of the type LTM-ETM-Metalloid, was chosen: $\text{Fe}_{74}\text{Mo}_4\text{P}_{10}\text{C}_{7.5}\text{B}_{2.5}\text{Si}_2$. A similar composition was presented by S.J. Pang at the ISMANAM 2007 Conference as being a composition which allows the preparation of BMGs up to 4 mm diameter and a length of 5 cm. We run some preliminary trials on this composition and we found that the GFA is very high, a diameter of 4 mm can be easily reached upon casting, even when dirty raw materials are used. Moreover, a fully amorphous rod with 5 mm diameter and 3 cm length was produced. So, the advantage of such alloy is the good GFA, expected to have a high saturation magnetization due to the high Fe content and also it seems to have rather good mechanical properties (not very brittle, which may enhance the application field). At the first glance, the presence of Mo can be a commercial disadvantage, because of its price, which is twice as high as the Co price, but for example in comparison with the FeCoBSiNb alloy it should be cheaper, because the quantity of Mo used is 4 times less than the Co amount. However, if for preparation of $\text{Fe}_{74}\text{Mo}_4\text{P}_{10}\text{C}_{7.5}\text{B}_{2.5}\text{Si}_2$ BMGs only industrial raw materials like FeP, FeB, FeSi, FeMo and graphite might be used (without lowering too much the GFA), it would assure its production at a competitive price.

2.3.3 New Alloys and their Compositional Design Strategy

It should be mentioned again that there doesn't exist an universal recipe which can be used in order to find new alloys able to retain the amorphous state. However, few things may help to find- or at least to tailor- the composition. For example, one can suppose that the addition of a big element which can act as "glue" atom (like Nb or Mo) in the complex Fe_{23}B_6 -type network may be helpful. Also, the addition of Y, for example, may help the glass formation by acting as an oxygen scavenger. Further are summarized the other compositions tried in this work, together with the respective reasons for which the respective compositions were developed, as well as a brief description of the main results, the details being presented later.

- Y-added alloys. It is shown in literature [Lu03b, Pon04] that Y may enhance the GFA by acting- eventually- as an oxygen scavenger, therefore acting toward the intrinsic cleaning the melt and removing the heteronucleants. We added Y to the $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$ master alloy but the new ob-

tained compositions did not show better GFA. These aspects are presented in subchapter 4.4.

- Following the route used to design the FeCoBSiNb BMGs, we tried to take other known composition which allows fabrication of thick amorphous ribbons and contains C (the reasons of introducing C is already mentioned). This is the $\text{Fe}_{77.5}\text{P}_{12.5}\text{C}_{10}$ alloy, which was reported to be amorphous up to a thickness of 360 μm [Ino82]. The target compositions was $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{77.5}\text{P}_{12.5}\text{C}_{10}]_{96}\text{Nb}_4$. The high content of P and C makes impossible the simultaneously use of pre-alloys FeC, FeP and FeNb. However, from the homogeneity reasons, at least FeP and FeNb pre-alloys must be used. Preliminary trials with $(\text{Fe}_{77.5}\text{P}_{12.5}\text{C}_{10})_{96}\text{Nb}_4$ and $[(\text{Fe}_{0.9}\text{Co}_{0.1})_{77.5}\text{P}_{12.5}\text{C}_{10}]_{96}\text{Nb}_4$ compositions show relatively good and reproducible results. The advantage of $[(\text{Fe}_{0.5}\text{Co}_{0.5})_{77.5}\text{P}_{12.5}\text{C}_{10}]_{96}\text{Nb}_4$ composition would be a new class of magnetic BMGs (due to the difficulties in preparation, this composition is not mentioned in literature up to now), with higher saturation magnetization and higher permeability.

Fe-Based Bulk Metallic Glasses

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