Thesis abstract

The actual habilitation thesis is a part of an extended research project conducted and performed by the author- and therefore the Leibniz Institute for Solid State and Materials Research (IFW) Dresden, Germany- for OCAS N.V. Zelzate, Belgium. OCAS (Onderzoeks Centrum voor de Aanwending van Staal, ArcelorMittal Global R&D Gent) is an advanced, market-oriented research center for steel applications. Based in Belgium, it is a joint venture between the Flemish Region and ArcelorMittal, the world's largest steel group.

The work is dedicated to the Fe-based bulk metallic glasses (BMGs). Generally, the BMGs establish a new class of advanced materials with amazing properties, discovered around 1988, and they are metallic alloys with amorphous structure. Among them, the Fe-based BMGs were synthesized for the first time in 1995 and since then tremendous efforts were put to create new classes of amorphisable alloys. Despite their relatively complicated chemical compositions, the low price of the used elements, as well as the possibility to use industrial pre-alloys, make the Fe-based BMGs very attractive for industrial application. Therefore, a clear image of what may affect the glass-forming ability (GFA) of these BMGs with the emphasis on the impurities which may be present in the master alloy is strongly required.

The thesis is structured in 7 Chapters and starts with theoretical consideration about metallic glasses. There the basic thermodynamical and kinetic aspects of the glass formation are presented, together with the historical development of BMGs in general and Fe-based BMGs in particular.

Chapter 2 presents the methodology and the model alloys chosen for investigations, as well as the strategy for assessing the GFA and the role of impurities. This must be done by corroborating experimental data obtained upon several types of investigations: differential scanning calorimetry, X-ray diffraction (room temperature and *in-situ* upon heating), magnetic measurements, high-resolution transmission electron microscopy (HR-TEM). As starting alloys $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ and $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ (at.%) were chosen. Further, it is proposed to assess the role of Yttrium additions (because it was shown in literature that Yttrium may enhance the GFA by acting- eventually- as an oxygen scavenger and, because of its big atomic radius, frustrating further the formation of the crystalline network). Following the route

used to design the FeCoBSiNb BMGs, the brand new $(Fe_{77.5}P_{12.5}C_{10})_{96}Nb_4$ and $[(Fe_{0.9}Co_{0.1})_{77.5}P_{12.5}C_{10}]_{96}Nb_4$ compositions are proposed as well.

Chapter 3 describes in details the experiments and their particularities, showing pictures of actually used devices. A consistent part is dedicated to the X-ray diffraction in transmission configuration using high intensity high-energy monochromatic synchrotron radiation, research field in which the author was a pioneer and has numerous highly cited contributions.

The experimental results are presented starting with Chapter 4. Here it is shown that in the case of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$, 8 dissimilar master alloys (plus few additional ones, but with ingredients and techniques as before) were prepared using different elements and pre-alloys. Their chemical composition, as well as the composition of the used pre-alloys, was analyzed. The actual chemical compositions of all master alloys are very close to the target composition, but the small deviations affect in different ways the results. Upon experimental assessment of the maximum rod diameter achievable by copper mold injection casting it is concluded that the alloy with the best GFA is the one made using pure elements. The thermal and magnetic behavior of several as-cast samples are presented in the very last details and the results are discussed in regard with the real chemical composition of the used master alloys.

The influence of Yttrium additions is discussed as well in Chapter 4. Despite the data presented in literature, it is concluded that in this actual case the Yttrium does not enhance the GFA. Then the influence of the casting atmosphere is evaluated. The casting experiments upon which the best results were obtained took place when the casting atmosphere was not very clean, i.e. by casting in air. The content of Oxygen and Nitrogen in selected samples were analyzed. Interesting, both Oxygen and Nitrogen content have a descendent trend as the partial air pressure in the casting chamber increases and the lowest values were found in the samples cast in air. However, there is no evident trend regarding the amorphicity and the Oxygen or Nitrogen content.

The studies of the $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ BMGs are continued in Chapter 5. There the time-resolved XRD and crystallization behavior is presented. By using the Kissinger approach, as well as the Johnson-Mehl-Avrami (JMA) plots, it was found that the activation energy for crystallization is around 536 kJ/mol, which is very high and therefore indicates a good thermal stability against crystallization. Also, the

Avrami exponent takes the average value of 1.43. Together with a short incubation time (i.e. less than one minute) it is concluded that the glassy samples crystallize through a primary crystallization reaction and the mechanism is athermal and diffusion controlled. These findings are proved further by the XRD studies and the primary phase which forms there is of the $Fe_{23}B_6$-type having an fcc-like structure and with a large lattice parameter of about 1.2 nm, including 96 atoms in its volume unit. Further it is seen that the as-cast BMGs may contain small nuclei, which do not affect the macroscopic properties. When the $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ samples do not become fully amorphous upon copper mold casting, the crystalline phases which form there are the equilibrium phases, not the metastable $Fe_{23}B_6$-type. Therefore, the foreign elements which may deteriorate GFA are those that stabilize the corresponding equilibrium crystalline phases.

The other model alloy, $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$, is analyzed in Chapter 6. 11 different master alloys were prepared using diverse combination of ingredients, pure elements and ferroalloys. The GFA of all master alloys was evaluated from experimental point of view and a ranking was established. This time the purity of the used ingredients does not play a very important role. Moreover, the master alloy needs a small content of foreign elements in order to retain the glassy state at room temperature, as for example Manganese. These important findings were patented, details are given in: Nele Van Steenberge, Daniel Ruiz-Romera, Mihai Stoica, Uta Kühn and Jürgen Eckert, world patent WO 2013087627 A1 or European patent EP2791376A1.

As for the FeCoBSiNb alloy, also in this case the detailed DSC and XRD analyses are presented. The crystallization behavior of $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ BMGs is much more complicated as the one find for $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ BMGs. Due to the complexity of crystallization, data from magnetic measurements were put together with the DSC and XRD results. Finally, it was found that the initially fully amorphous sample crystallizes through several exothermic events, forming first fcc γ-Fe, together with Mo-P, Mo-C, Mo-B and/or Mo-Si. The residual amorphous matrix crystallizes then through the formation of $(Fe,Mo)_3P$, which will coexist with already formed Mo-P, Mo-C, Mo-B and/or Mo-Si. At the end the fcc γ-Fe will transform in bcc α-Fe (event clearly visible upon thermomagnetic measurements), the $(Fe,Mo)_3P$ will be depleted in Mo, some $Fe_{23}B_6$ forms (consuming Fe from its γ phase) plus whatever quantities of Mo-P, Mo-C, Mo-B and/or Mo-Si.

Transferring the knowledge accumulated by studying the role of the impurities on the glass-formation in the case of $[(Fe_{0.5}Co_{0.5})_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ and $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ alloys, two new BMG forming alloy compositions were designed: $(Fe_{77.5}P_{12.5}C_{10})_{96}Nb_4$ and $[(Fe_{0.9}Co_{0.1})_{77.5}P_{12.5}C_{10}]_{96}Nb_4$. The master alloys are prone to form NbC and this was seen in few cases. However, after optimization of the fabrication procedure, as well as by partial substitution of Fe with Co, the amount and the dimensions of the intermetallic NbC is drastically reduced. Therefore, the master alloy should be made in two steps: eutectic 25Fe 75Nb (wt.%) by arc-melting and then FeP pre-alloy together with pure Co, eutectic FeNb and graphite particles can be melt in induction furnace. As a possible development toward industrial up-scaling, the industrially known procedure of arc melting with a consumable graphite electrode may be used. In this way a higher amount of Carbon can be alloyed and the formation of carbides could be avoided.