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FeNbB BULK METALLIC GLASS WITH HIGH BORON CONTENT

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Abstract. Fe-based alloys able to form magnetic bulk metallic glasses (BMGs) are of the type transition metal – metalloid and often contain 5 or more elements. Usually, the metalloid content is around 20 at.%. Very recently, the $Fe_{66}Nb_4B_{30}$ alloy was found to be able to form BMG by copper mold casting, despite its high metalloid content. Before casting, the arc-melted master alloy was cleaned by fluxing with B_2O_3. The BMGs of this composition can be prepared in rod-shape and the maximum diameter for which the alloy is still amorphous is 2 mm.

Several compositions with boron contents around 30 at.% or even higher were calculated since 1993 as possible compositions of the remaining amorphous matrix after the first stage of nanocrystallization of Finemet-type $Fe_{77}Si_{14}B_9$ glassy ribbons with 0.5 to 1 at.% Cu and a few percent Nb addition. Melt-spun ribbons of all calculated compositions were found to be glassy. The composition of the ternary Fe-based BMG investigated in the present study resulted as an optimization of all possibilities. The alloy is ferromagnetic with a Curie temperature T_c = 550K, a glass transition temperature T_g = 845K, a crystallization temperature T_x = 876K, a liquidus temperature T_{liq} = 1530K and a mechanical strength of 4 GPa. The as-cast samples show a very low coercivity of 1.5 A/m, and a saturation of around 1 T.

1. INTRODUCTION

Fe-, Co- or Ni- based metallic glasses are good candidates for application as soft magnetic materials because of the lack of crystal anisotropy [1]. Although conventional soft magnetic alloys may have higher saturation magnetization compared to ferromagnetic metallic glasses [2], the latter often have very high mechanical strength and high resistance against corrosion, which is important for application as magnetic parts in valves, clutches, or relays. As a result of the requirement for vitrification, the ferromagnetic bulk metallic glasses (BMGs) should be cooled at around 10^2-10^3 K/s [3] and this limits the samples diameter and thickness to only a few millimeters. In 2004, Ponnambalam *et al*. [4] and independently, Lu *et al.* [5] succeeded to cast (Fe-Cr-Co-Mo-Mn-C-B)-(Y,Ln) BMGs with a thickness as large as 10 mm (Ln stands for lanthanide elements). However, those glasses are ferromagnetic only at low temperature, with a Curie temperature of around 30-55K (depending on the composition). The largest diameter, 12 mm, was obtained for an $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ alloy but these 'bulk amorphous steels' cannot be used as magnetic parts at room temperatures.

Despite their unique properties, BMGs are currently used only in few practical applications. One

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of the main reasons is the production cost, which is still high due to the cost of the raw materials (Pd, Zr, Ti, *etc.*) and costs related to the purification of such elements. The difficulty of working with very reactive elements (Ln, Y, Nd, *etc.*) is also an impediment. These problems could be solved by using cheap (low purity) raw materials, but this usually decreases the glass-forming ability (GFA), or by reducing the number of constituent elements. One such composition is FeNbB with a boron content of around 30 at.% [6]. Few older studies [7,8] discuss the glass formation, the structure upon crystallization and the magnetic properties of glassy ribbons of compositions $Fe_{70-x}Nb_xB_{30}$ with x = 2, 4, 6, 8, and 10 or more recently [9,10], for $Fe_{90-x}Nb_{10}B_x$ with x = 10, 20, and 30, but there have been no data on the formation of BMGs from these alloys and the available data for glassy ribbons do not predict such possibility. For concentrations of Nb below 4 at.%, they do not display a clear glass transition event upon heating at a constant rate [7]. A further increase of the Nb content leads to the appearance of a supercooled liquid region $\Delta T = T_x - T_g$ (where T_x and T_g are the crystallization and glass transition temperatures, respectively) of about 30K wich extends up to 60K for 10 at.% Nb [8] but the magnetic properties deteriorate: the polarization at saturation J_s decreases from 1 T for 4 at.% Nb to 0.3 T for 10 at.% Nb [8]. In fact, Yavari *et al.* [7] demonstrated that the niobium content is the main determining factor for the Curie temperature T_c, as well as for the crystallization temperature T_x: as the Nb content increases, T_c decreases and T_x increases. Very recently [6], we reported that the $Fe_{66}Nb_4B_{30}$ alloy may form BMG by copper mold casting. The BMGs of this composition can be prepared in rod-shape and the maximum diameter for which the alloy is still amorphous is 2 mm. Before casting, the arc-melted master alloy was cleaned by fluxing with B_2O_3. The present study aims to present the preparation of the $Fe_{66}Nb_4B_{30}$ fully amorphous BMGs and to discuss their thermal stability, mechanical behavior and magnetic properties.

2. EXPERIMENTAL

The ternary $Fe_{66}Nb_4B_{30}$ master alloy examined in this study was obtained by arc-melting Fe and Nb metals together with crystalline B in a Ti-gettered Ar atmosphere. The ingot was further fluxed with B_2O_3 in order to remove oxide impurities as much as possible. The fluxing was performed under high vacuum in an induction furnace in two steps, each one not shorter than 60 minutes. Several BMGs of the composition $Fe_{66}Nb_4B_{30}$ were cast by injecting the molten alloy into copper molds in order to obtain rods with smallest diameter of 1 mm and largest diameter of 2 mm. The total rod length was 4 cm. The appearance of the cast BMGs and the used copper molds was presented in a previous study [6]. The glassy nature of the BMGs was examined by X-ray diffraction in transmission configuration using a high intensity monochromatic synchrotron beam (with wave length of 0.0155 nm) at ID11 at ESRF Grenoble. The thermal stability was examined by differential scanning calorimetry (DSC) at a constant heating rate of 20 K/min. The hardness of the BMG was measured using a Vickers hardness tester equipped with a diamond rectangular prism under different values of applied load: 1.96 N, 2.94 N, and 4.9 N, respectively. The load was maintained for 10 s. The specimen was embedded in an acrylic resin and polished plane-parallel. The measurements were performed along the sample axis. In order to have a good resolution, the results were averaged for sets of 10 indents. The compresion behavior was checked using an INSTRON electromechanical device under a constant strain rate of 0.008 s^{-1}. The Curie temperature and the saturation magnetization were measured using a vibrating sample magnetometer (VSM). For Curie temperature measurement, a small slice cut from 1 mm diameter rod was heated up to 900K in a DC magnetic field high enough to

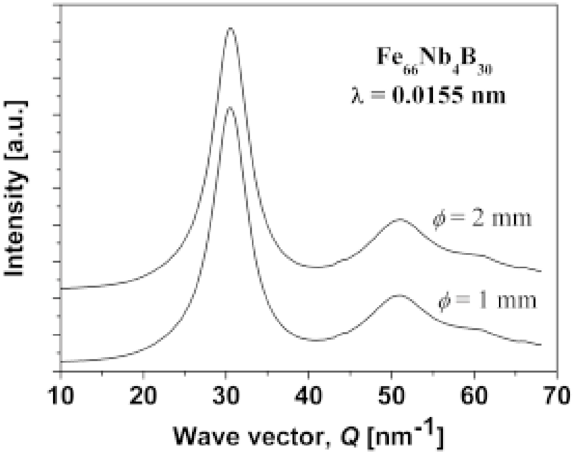

Fig. 1. X-ray diffraction patterns taken in transmission configuration for $Fe_{66}Nb_4B_{30}$ BMGs with 1 and 2 mm diameter.

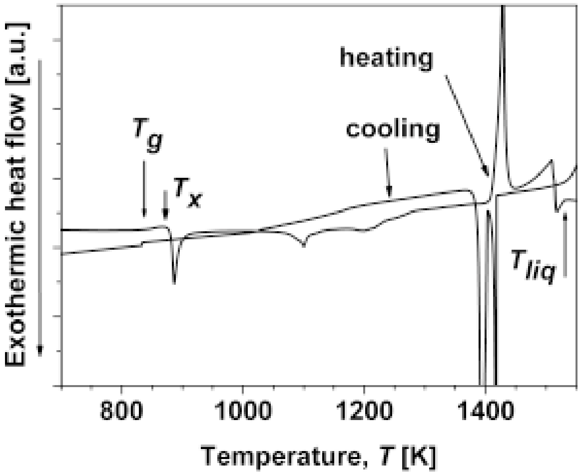

Fig. 2. DSC traces measured at 20 K/min heating rate for the 1 mm diameter $Fe_{66}Nb_4B_{30}$ BMG showing the glass transition, crystalization, melting and solidification.

saturate the sample. The coercivity was measured with a Förster Coercimat under a DC applied field of 200 kA/m.

3. RESULTS AND DISCUSSION

In order to find the composition capable to vitrify as BMG, Inoue proposed three empirical rules derived from kinetic and thermodynamic considerations [3,11]: atomic size difference of at least 12%, presence of at least three atomic species and attractive interactions (negative heats of mixing). The metallic glass compositions of the present study conform to these requirements: there are three constituents, the constituents have a difference in atomic size ratio of more than 12% [12] and strong negative heats of mixing except for Fe-Nb [13]. Once the kinetic and thermodynamic requirements are fulfilled, the only hindrances which can limit the glass-forming ability (GFA) are the impurities present in the melt [14]. Such impurities can be oxides particles that can act as sites for heterogeneous nucleation. A viable method to clean such Fe-based alloys is to melt them together with B_2O_3 [14,15]. This method was applied to purify the arc-melted $Fe_{66}Nb_4B_{30}$ ingots. After fluxing, the remaining boron oxide was carefully removed and the ingots were used for copper mold casting. In this way the ternary Fe-based BMG was obtained.

Fig. 1 shows the X-ray diffraction patterns for rods with 1 and 2 mm diameter. The patterns consist only of broad diffraction maxima centered at $Q = 30.50 \pm 0.02$ nm^{-1} and $Q = 50.89 \pm 0.02$ nm^{-1}, which is characteristic for an Fe-based amorphous alloy of the transition metal-metalloid type. No traces of additional Bragg peaks are present. Q is the wave vector, which is equal to $2\pi/d$, where d is the spacing between the atomic planes of the material. The samples were in fact checked every 1 mm along the rod length but for simplicity only two diffraction patterns are presented. The other known multi-element Fe-based BMGs [16] show similar X-ray diffraction patterns. For example, the wave vector corresponding to the first broad maximum of the $Fe_{65.5}Cr_4Mo_4Ga_4P_{12}C_5B_{5.5}$ BMG is $Q = 30.51 \pm 0.08$ nm^{-1} [17], a value which is comparable with the values measured for the present alloy. Metallic glasses are amorphous or non-crystalline materials characterized by the absence of long-range translational order typical of crystalline solids. However, they possess well defined short-range and medium-range order structure over a few atomic distances [18]. A higher value of Q corresponds to shorter average interatomic distances and indicates a higher atomic packing density of the BMG.

Fig. 2 shows the DSC traces of the $Fe_{66}Nb_4B_{30}$ BMG. The offset of the glass transition, which is at 845K, is considered to be the glass transition temperature T_g. Crystallization takes place through a single exothermic reaction at T_x = 876K. As it is seen from the DSC curves, the melting takes place through a peritectic reaction. The liquidus temperature, T_{liq}, measured as the onset of the last melting peak, is 1530K. The width of the supercooled liquid region, $\Delta T_x = T_x - T_g$ is 31K and the reduced glass transition temperature T_{rg}, defined as T_g / T_{liq}, is 0.55. The crystallization temperature of the BMG is lower than that measured for ribbons with the same composition (900K found by Itoi and Inoue [8]). The differences between rod and ribbons can be caused by slight differences in compositions which may arise upon fluxing experiments. During the fluxing, the alloy is kept long time at 50K over its liquidus temperature under high vacuum (10^{-6} mbar). In these working conditions, a partial evaporation, which can shift the starting overall composition, may be expected. The supercooled liquid region width ΔT_x = 31K and the reduced glass transition temperature of 0.55 are values characteristic of alloys with relatively good GFA [11] but are nevertheless lower than those reported for some Pd- or Zr-based BMGs which may vitrify at a critical cooling rate even below 1 K/s [3].

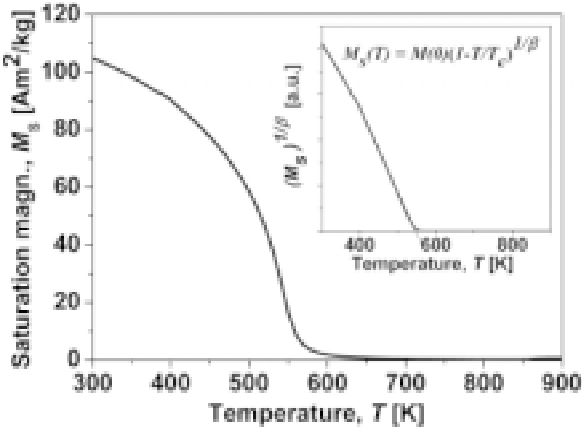

Fig. 3. The variation of saturation magnetization M_s as a function of temperature. The inset shows in detail the Curie temperature determination. The measured sample was cut from 1 mm diameter BMG.

The glass transition temperature of 845K shown by this ternary BMG is much higher than in non-ferrous BMGs [19], and is comparable to other Fe-based BMGs, as for example $(Fe_{0.75}B_{0.15}Si_{0.1})_{96}Nb_4$ [19] or $Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$ [4]. If we consider that a higher T_g reflects a stronger nature of the bonding between the constituents elements, this ternary BMG should have very high mechanical strength. In the case of other Fe- or Co-based BMGs, the available experimental data for the fracture strength σ_f, measured in compression, follows a linear relation with T_g [17]: $\sigma_f = -7.200 + 13.2 \cdot T_g$, where σ_f is given in MPa and T_g in K. According to this equation, the fracture strength of the $Fe_{64}Nb_4B_{30}$ BMG should be around 4 GPa. If we consider also the relation $\sigma_f = HV / 3$ [20], the Vickers hardness HV should be 12 GPa (or 1224). The experimental results follow this theoretical approach. The average value for HV is 11.7 GPa (or 1200) and upon compresion the samples fracture at 3.8 GPa, in good agreement with the empirical relation.

The main applications of Fe-based metallic glasses are as soft magnetic materials. The $Fe_{66}Nb_4B_{30}$ glassy ribbon shows good magnetic properties: a coercivity H_c of 4 A/m, a polarization at saturation J_s of around 1 T, a saturation magnetostriction constant λ_s of 16 ppm and a magnetic permeability μ_e at 1 kHz of 17 000 [8]. The value of H_c depends mostly on surface and volume pinning of magnetic domain walls [21]. Due to surface irregularities, H_c is proportional to the ratio of the surface roughness amplitude to the specimen thickness. This contribution to H_c should be rather low for bulk samples, lower than in the case of ribbons, because the surface upon casting is very smooth and without scratches, even on the nanometer scale, and the thickness is significantly larger than that of rapidly quenched ribbons. The contribution to H_c due to volume pinning results from the presence of internal stresses or quenched stresses the magnitude of which depends primarily on the coefficients of thermal expansion and thermal conductivity and the specimen thickness.

The as-cast $Fe_{66}Nb_4B_{30}$ BMG studied in the present work shows a DC coercivity of 1.5 A/m and a saturation magnetization at room temperature around 105 Am^2/kg. The estimated density is ρ = 7.542 g/cm^3 and with this value of density, 105 Am^2/kg corresponds to a polarization of 1 T. Fig. 3 shows the variation of saturation magnetization M_s as a function of temperature. As it is known from literature, for temperatures close to T_c the saturation magnetization can be described by [22]: $M_s(T) = M_s(0)(1-T/T_c)^{1/\beta}$, with the exponent $\beta = 0.36$. In order to minimize the error, the experimental results were plotted as $(M_s)^{1/\beta}$ versus T (the inset of Fig. 3). The Curie temperature was considered the temperature where the $(M_s)^{1/\beta}$ deviates from linearity (see the straight line which cut the temperature axis in the inset of Fig. 3). From there the Curie temperature T_c was found to be around 550K.

4. SUMMARY

The present study reports a ternary glass-forming composition of the type FeNbB with 30 at.% boron and 4 at.% Nb content. This type of composition was obtained in 1993 by calculating the possible compositions and analyzing the properties of the remaining amorphous matrix upon nanocrystallization of Finemet-type $Fe_{77}Si_{14}B_9$ with Cu and Nb additions. Using new approaches developed in the last years, a new ternary $Fe_{64}Nb_4B_{30}$ BMG was obtained by copper mold casting. The glassy nature of rod-shaped specimens was confirmed by X-ray diffraction in transmission and the thermal stability was studied by differential scanning calorimetry. The high fracture strength of nearly 4 GPa and a hardness of almost 12 GPa, combined with very good soft magnetic properties - coercivity of 1.5 A/m and saturation of 1 T - make this alloy highly promising for future application.

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