The effect of Ni-substitution on physical Properties of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ Bulk Metallic Glassy Alloys

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ABSTRACT

We have succeeded in producing bulk metallic glass by partial substitution of Fe with Ni in Fe-B-Nb alloys which could otherwise be only melt spun into amorphous ribbons. Substitution by Ni in the $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ alloys with ($x \sim 2, 4, 6, 8, 10, 12$ and 14) improves the glass forming ability of the materials and as a result rods of same compositions can be fabricated. Magnetically the BMG alloys remain soft with coercivity below 500mOe. However, the electrical resistivity of the system decreases significantly by as much as a factor of two with the increase of Ni concentration, and becomes more metallic like with a positive temperature coefficient.

INTRODUCTION

It is well known that although multi component Fe based amorphous ribbons can be melt spun it is not obvious that for the same composition we can obtain Bulk metallic glasses (BMG). Methods to enhance the glass forming ability to obtain BMGs of the same composition is thus a topic attracting considerable attention from both fundamental as well as the application point of view [1–12]. The kinetics of phase transformation along with the growth mechanism of glass formation is an intriguing subject for the fundamental studies [13, 14]. Since BMG materials often have exceptional mechanical strength, corrosion resistance and excellent soft magnetic properties they are plausible candidates for a variety of electrical and electronic component development [1–12]. One important objective is to develop BMG materials with larger cross sections without losing their excellent properties of the glassy state. The ability to fabricate BMGs with larger cross section for a BMG is closely related to its glass forming ability (GFA). In this regard, Inoue put forward three empirical rules [4] for better stabilization of the glassy state: (a) the alloys should have at least three constituent atoms. (b) the atomic size difference between component elements must be greater than 12% and (c) the constituent elements must have large negative heat of mixing. These criteria have led to the synthesis of a large number of BMGs with cross sections from a few mm to even few tens of mm. However, despite following Inoue's rules, why some alloys can easily be cast into BMG while others can not is not well understood.

Fe-based BMGs are particularly interesting because they show almost square hysteretic loops with quite large saturation magnetization and rather small coercivity [8, 11]. Generally Fe-based alloys have low GFA and poor thermal stability, which are disadvantageous to produce BMGs [8]. This work is an investigation on determining how the properties of a Fe-based system modified on partial substitution of Fe with Ni. We have prepared alloys of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x \sim 2, 4, 6, 8, 10, 12$ and 14) and studied their thermal, electrical transport and magnetic properties. A striking result is that the GFA is significantly improved due to the addition of Ni. As a consequence, BMG rods with diameter ~ 0.5 mm have been cast for these compositions, which is hardly possible with $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$ [8].

EXPERIMENTAL DETAILS

Master alloys of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ were synthesized by induction melting of constituent elements with purity $\sim 99.9\%$. Melting was carried out in Ar-atmosphere in the presence of Titanium getter. The ribbons of these materials with thickness $\sim 20\mu\text{m}$ were fabricated by melt spinning method from the Ni substituted master alloy. We also prepared rods of similar composition with diameter of 0.5mm using Cu-mold casting technique in Ar-atmosphere. The X-ray diffraction (XRD) study was carried out on ribbons and rods. Beside XRD study, the magneto-thermo-gravimetric analysis (MTGA) technique was used to probe the phase purity of the samples. The thermal characterization study of the prepared ribbons was carried out by differential scanning calorimetry (DSC) at the heating rate of 0.67 K/s with the samples in a constant flow of highly pure Ar atmosphere. The differential thermal analysis (DTA) of the ribbons was carried out at the heating rate ~ 0.17 K/s after complete melting to obtain their liquidus temperature (T_l), and melting temperature (T_m). The magnetic properties of the sample were studied using a Foner type vibrating sample magnetometer (VSM). A conventional four probe technique was employed for studying electrical transport properties of the samples.

RESULTS AND DISCUSSIONS

The X-ray diffraction (XRD) patterns of the ribbons points out their amorphous structure. Beside XRD study, the MTGA study of the ribbons confirms the purely amorphous nature of the ribbons and non-existence of any possible crystallinity (Fig. 1 a). From DSC analysis, the glass transition temperature (T_g), crystallization temperature (T_x) for the ribbons have been determined (see table I). Moreover the DSC traces (Fig. 1 b) indicate the presence of the super cooled region ($T_x = T_x - T_g$) confirming the formation of glassy state in the samples. The liquidus temperature (T_l), and melting temperature (T_m) were obtained from DTA study.

Figure 1. (a) MTGA curve for $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x=4$) amorphous ribbon. (b) DSC traces for the amorphous ribbons.

There are many studies regarding the criteria of glass forming ability (GFA) of materials [4–7]. During the cooling of liquid alloy from the molten state down to T_g , the viscosity of the melt increases to a high value giving rise to the formation of glass. Therefore alloy with high value of T_g and low value of T_l is preferable for the formation of glass [5]. Turnbull explored the point by defining a parameter called reduced glass transition temperature ($T_{rg} = T_g/T_l$) [5]. For becoming glass, alloy must have T_{rg} equals to 0.4 and the glass formation would be easier as T_{rg} of the material increases [5]. Although T_{rg} deals with the condition of glass formation, it does not address the stability of the glass. It has been suggested that T_x is a crucial parameter in determination of the stability of glassy state and GFA of material scales up with T_x [4]. In this

context, Lu and Liu [6] argued that the parameter of GFA must reflect not only the condition of glass formation but also its stability [6]. They developed a parameter, $\gamma = T_x / (T_l + T_g)$ [6]. More recently, Chen et al. derived another parameter of GFA, $\delta = T_x / (T_l - T_g)$, [7] as well. All those parameters are calculated for the present ribbons and mentioned in table II. For $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x \sim 4, 6, 8, 10, 12$ and 14) ΔT_x , T_{rg} , γ and δ (table-II) increase in comparison with unsubstituted $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$. In the case of sample with $\sim 2\%$ Ni, except ΔT_x and γ , all the other parameters are larger than that for unsubstituted compound. For $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$, ΔT_x , T_{rg} , γ and δ are 39 K, 0.559, 0.375 and 1.327 respectively [8]. From the thermal analysis of the samples, it can be concluded that the substitution of Ni excels the ability of glass formation.

Table I. T_g , T_x , and ΔT_x of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ with different concentration of Ni as determined from thermal analysis by DSC

Ni (%)	T_g (K)	T_x (K)	ΔT_x (K)
2	838	874	36
4	829	871	42
6	830	870	40
8	827	866	39
10	824	867	43
12	817	863	46
14	811	854	43

The enthalpies of mixing between Ni with B and Nb are large and negative. For example, the estimated mixing enthalpies of equal molar atomic pairs of Ni-B and Ni-Nb are -24kJ/mol and -30kJ/mol respectively [17]. It seems that large values of mixing enthalpies of Ni with Nb and B result in the improvement of GFA due to the substitution of Ni in Fe-site of $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$ as pointed out by Inoue [9].

Table II. T_{rg} , γ and δ for $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ with different concentration of Ni obtained from DTA data

Ni (%)	T_{rg}	γ	δ
2	0.561	0.375	1.334
4	0.564	0.379	1.359
6	0.573	0.381	1.405
8	0.601	0.393	1.575
12	0.567	0.382	1.385
14	0.575	0.385	1.426

The magnetic field dependence of magnetization (M-H) at 300 K for the ribbons exhibit typical square loops of a soft ferromagnetic with negligible coercivities (Fig. 2a) is a typical example indicating their soft magnetic properties and also large saturation magnetization (M_s). The M_s of the ribbons $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ with concentration varying from $x \sim 2$ to 14 decreases from $\sim 136 \text{ emu/g}$ to 118 emu/g . The coercive fields (H_c) for all the samples are below 0.5 Oe , and the smallest H_c ($\sim 0.26 \text{ Oe}$) was obtained for the ribbon with Ni-concentration $\sim 8\%$ (see inset of Fig. 3). Such small H_c along with large M_s of the samples gives rise to the possibility of using them in the soft magnetic applications.

Figure 2. (a) Magnetic field dependence of magnetization for $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x \sim 2, 4, 6, 8, 10, 12$ and 14) ribbons. Insets: at top H_c and M_s of different ribbons plotted with respect to Ni content. At bottom M-H curve in low magnetic field region for ribbon with Ni concentration = 8% showing coercivity $\sim 0.26 \text{ Oe}$, which is the lowest among the samples studied in present work. (b) The temperature dependence of resistivity for the ribbons with $x = 2, 6, 12$, and 14 .

The electrical transport measurements on the ribbons were performed in the temperature range $77\text{--}300 \text{ K}$ by a conventional four probe method. While the almost temperature independent is typical characteristic of amorphous materials, substitution with Ni is found to significantly lower the absolute value of the resistivity and also temperature coefficient becomes more and more positive as seen especially for the $x=14$ sample in the figure 2(b). According to Mooij's relation, the alloys with resistivity less than $\sim 150 \text{ microhm-cm}$ at room temperature can have positive value of the temperature co-efficient of resistivity (TCR) [15]. Clearly our results seen in figure 2 (b) are consistent with the Mooij's empirical observation.

Figure 3. X-ray diffraction pattern for $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x \sim 4$, and 12) rod showing amorphous structure. Inset: the MTGA graph for $\text{Fe}_{68}\text{B}_{24}\text{Nb}_4\text{Ni}_4$

We have successfully developed rods of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ with diameter of 0.5 mm. The formation of rod with unsubstituted $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$ is hardly possible [8]. Hence the success in synthesizing of rod can be considered as the direct experimental evidence of the improvement in glass forming ability due to the substitution of Ni. The amorphous structure of rods is confirmed by XRD as well as MTGA study. Typical example of the XRD patterns of $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x = 4$ and 12) rods are shown in Fig. 3. The inset in fig 3 is the MTGA trace for the rod with $x = 4\%$ shows the expected sharp kink near T_c the magnetic transition temperature. Similar to ribbons, the rods also exhibit very small hysteresis in M-H loop (Fig. 4) with decreasing M_s with the substitution of Ni concentration. The value changes from ~ 138 -128 emu/g for the sample with $x \sim 2$ to 14%. The M_s and H_c values obtained for rods are also comparable to those for ribbons.

Figure 4. Magnetic field dependence of magnetization for $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$ ($x \sim 2, 4, 8, 12$ and 14) rods.

CONCLUSION

We have shown that partial substitution of Ni significantly improves the glass forming ability in $\text{Fe}_{72-x}\text{B}_{24}\text{Nb}_4\text{Ni}_x$. As a result, the fabrication of rod of diameter ~ 0.5 mm has been possible in all the studied compositions which would be rather impossible in the case of $\text{Fe}_{72}\text{B}_{24}\text{Nb}_4$. The electrical resistivity of the system is significantly reduced with the increase in Ni concentration and the temperature coefficient accordingly becomes more and more metallic like. Another notable property of the system is the manifestation of very small coercivity ($H_c < 500\text{mOe}$) and high M_s which indicates their possible applications as potential soft magnetic materials.

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