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Fe–Y–M–B (M = Nb or Ta) bulk metallic glasses with ultrahigh strength and good soft magnetic properties

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Abstract
The effect of partial replacement of Y with a fourth element (Nb or Ta) on the glass forming ability (GFA), mechanical, thermal and magnetic properties of ternary Fe–Y–B bulk metallic glasses (BMGs) was explored. GFA, thermal, magnetic and mechanical properties of BMGs with compositions Fe72Y6−xMxB22 (M being Nb or Ta, x = 1–5) were investigated. The partial replacement of Y by Nb or Ta greatly enhances the GFA to cast glassy rods with a diameter of at least 4 mm (Nb) or 3 mm (Ta) from the original 2 mm. They exhibited high saturation magnetization above 1.25 T and low coercivity below 20 A m−1. The Curie temperature and electrical resistivity are higher than 530 K and 190 µΩ cm, respectively. The Fe72Y4M2B22 (M = Ta or Nb) BMGs show ultrahigh compressive strength of 4150–4200 MPa. With lower content of Y, which is very reactive, and the combination of promising properties, these new BMGs have potential for industrial applications compared with the ternary Fe–Y–B BMGs.

1. Introduction
The discovery of iron-based amorphous magnetic alloys have drawn much attention due to their good soft magnetic properties for industrial applications in transformers and cores. Since 1988, many bulk metallic glasses (BMGs) have been developed in multi-component Mg-, lanthanide-Zr-, Pd- and Ti-based alloy systems [1–6]. These BMGs inevitably show a wide super-cooled liquid region that quantifies the degree of resistance against crystallization leading to a high glass forming ability (GFA). They exhibit many promising mechanical or functional properties. For iron-based alloys, it has been desirable to explore ones with better GFA to cast Fe-based BMGs with sound magnetic properties to extend their industrial applicability. For iron-based alloys, it has been desirable to explore ones with better GFA to cast Fe-based BMGs with sound magnetic properties to extend their industrial applicability. Inoue elucidated three empirical rules that govern the GFA of an alloy system: (1) multi-component alloys consist of more than three elements; (2) large difference in atomic size ratios larger than 12%; and (3) large negative heats of mixing [7]. According to these rules, new Fe-based BMGs have been successfully developed. They are mainly of the three groups of elements: Fe–(Al, Ga)–(P, Si, B, C) [8], Fe–(Co, Ni)–M–B (M = Zr, Hf, Nb, Ta, Mo, W) [9] and Fe–Ni–P–B [10]. However, these alloys are of complex composition with at least four constituent elements. Recently, simple ternary iron-based bulk glassy alloys containing only three elements, R–Fe–B, where R = Sc, Y, Dy, Ho and Er, were disclosed where the R content is only around 6 at% [11, 12]. Among these ternary iron-based bulk glassy alloys, the Fe–Y–B alloys show the best potential in applications due to the cheaper Y cost (compared with the other four rare-earths) and good soft magnetic properties (such as high saturation magnetization above 1.5 T). However, the high oxidation tendency of Y at high temperature causes inconvenience in alloy preparation during industrial processing, such as the need of a vacuum melting environment. It was hence desirable to ease the processing capability by reducing Y content while keeping the original properties (GFA, magnetic, etc) at least unchanged. The strategy we adopted was to partially replace Y with a fourth element, Nb or Ta, and the effects were...
investigated. The bulk GFA of the Fe–Y–B ternary system has been investigated in detail and disclosed elsewhere. The composition chosen for this investigation was Fe72Y6B22 which exhibits the best GFA (at least 2 mm glassy rods) among Fe–Y–B compositions [11, 12]. Subsequently, we modified the Fe–Y–B alloys with a transition metal, Nb or Ta. During our research, we noted a similar study of Fe77−YNb6B17Yz (z = 0–4) BMGs published in the literature [13]. However, our results turned out to be quite unique compared with theirs as will be disclosed in detail below.

2. Experimental

Multi-component alloy ingots with the nominal compositions Fe72Y6−xNxB22 (x = 1–5) and Fe72Y6−yTa1B22 (y = 1–4) were prepared by arc melting the mixture of pure Fe, Y, Nb, Ta metals and B beads (all with at least 99.9% purity) in an argon atmosphere. Amorphous ribbons with a cross section of 0.03 × 10 mm² were also prepared by a single-roller melt-spinning method. Bulk alloys in rod form with different diameters were prepared by a copper-mould injection-casting method. The structure of the as-cast ribbons and rods was examined by x-ray diffraction (XRD) using Cu Kα1 radiation. The thermal properties were studied by a differential thermal analyzer (DTA) at a heating rate of 0.33 K s⁻¹. The magnetic properties were measured with a vibrating sample magnetometer (VSM). The Curie temperature (Tc) was measured by a magnetic thermal-gravimetric analyzer (M-TGA) at a heating rate of 5 K min⁻¹. The electrical resistivity was measured by a typical four-point probe method on melt-spun ribbons. The micro-hardness was measured by a micro-Vicker hardness tester. The mechanical properties were measured with an Instron testing machine in a compression mode. The gauge sample was 2 mm in diameter and 3 mm in length. The strain rate was 5 × 10⁻⁴ s⁻¹.

3. Results and discussion

Figure 1 shows the XRD patterns taken on the cross section of as-cast rods of Fe72Y6−xNxB22 and Fe72Y6−yTa1B22 alloys with different diameters. The GFA increases from the capability of forming 2 mm diameter bulk glassy rods for Fe72Y6B22 (x = 0) to the maximum GFA of forming 4 mm and 3 mm diameter BMG rods as x = 2.3 and y = 1.2, respectively. Both Nb and Ta greatly improve the GFA of the Fe–Y–B alloys. The GFA of our Fe72Y6Nb6B22 is better than that of Fe77−YNb6B17Yz (x = 0–4) alloys published recently in the literature in which the best GFA was formation of 3 mm BMG rods [13]. The critical cooling rate (Rc) for the quenched alloys can be estimated by

\[ R_c \ (K \ s^{-1}) = dD/dt = 10/D^2, \]

where D is the cast diameter of the sample in cm [14]. Rc for our Fe72Y6Nb6B22 BMG is 63 K s⁻¹, while for Fe77−YNb6B17Yz in the literature it is 111 K s⁻¹. This discrepancy comes from the difference in boron content. Five per cent more B content in our BMGs causes a lower critical cooling rate. This will be further elucidated below.

The Nb-modified BMG, Fe–Y–Nb–B, is the largest BMG available in quaternary Fe-based alloys reported to date. The results show that the partial Nb (2 at%) or Ta (1 at%) substitution has a great effect in improving GFA of the Fe–Y–B ternary alloys. In an opposite substitution, the GFA of Fe–Nb–B and Fe–Ta–B alloys is noticeably enhanced by the addition of 2–4 at% Y. It results in a manifest improvement in forming bulk glassy rods, while in Y-free ternary alloys, such as Fe72Nb6B22 and Fe72Ta6B22, the GFA is so low as to attain amorphous state only in melt-spun thin ribbon form. These results also agree well with the aforementioned literature which investigated the effect of Y addition in Fe–Nb–B ternary alloy [13]. In that study Y was taken as an oxygen scavenger to greatly improve GFA of the Fe–Nb–B alloys, not as the main glass-former as in the current study. The dual addition of Y and Nb (or Ta) has been elucidated to have an enormous positive effect on GFA of the Fe–B binary alloys [13]. The addition of Nb or Ta in the Fe–Y–B alloy also agrees with the three empirical rules elucidated in the introduction. Nb or Ta which is the second largest atom in the constituent elements (where the empirical rules elucidated in the introduction. Nb or Ta which agrees with the three empirical rules elucidated in the introduction. Nb or Ta which) substitution has a great effect in improving GFA of the Fe–Y–B ternary alloys are a much complicated network-like structure due to the extremely large difference in atomic sizes such that BMGs are possible with very simple ternary compositions [11]. The replacement of Y by Nb or Ta does add to the complexity of the amorphous networks, hence improved GFA. Comparing the published results [13], the higher B content in our alloys seems to be the main reason for higher GFA due probably to the stabilization of the amorphous structure because of higher Fe–B trigonal content of the alloys. That is to say, it is interesting to optimize the B content in...
exploring the quaternary Fe–Y–M–B BMGs with even higher GFA. Work is under way both theoretically and experimentally.

Figure 2 shows DTA curves of the Fe$_{72}$Y$_{6-x}$Nb$_x$B$_{22}$ and Fe$_{72}$Y$_{6-y}$Ta$_y$B$_{22}$ glassy ribbons. Due to increasing Nb or Ta content, the crystallization mode of the BMGs gradually changes from a multi-stage to a single-stage crystallization behaviour. The single-stage crystallization also plays an important role in achieving high thermal stability and better GFA as has been thoroughly investigated earlier by Inoue et al [19]. This phenomenon reveals that all crystalline phases crystallize simultaneously at the same elevated temperature so that it requires a long-range diffusion of constituent elements to achieve crystallization, leading to difficulty in crystallization processes. With these mentioned multi-effects working together, the GFA as has been thoroughly investigated earlier by Inoue et al [19].

Figure 3 shows the variation of thermal properties of amorphous ribbons with compositions Fe$_{72}$Y$_{6-x}$Nb$_x$B$_{22}$ and Fe$_{72}$Y$_{6-y}$Ta$_y$B$_{22}$ glassy rods. Due to increasing Nb or Ta content, the crystallization mode of the BMGs gradually changes from a multi-stage to a single-stage crystallization behaviour. The single-stage crystallization also plays an important role in achieving high thermal stability and better GFA as has been thoroughly investigated earlier by Inoue et al [19]. This phenomenon reveals that all crystalline phases crystallize simultaneously at the same elevated temperature so that it requires a long-range diffusion of constituent elements to achieve crystallization, leading to difficulty in crystallization processes. With these mentioned multi-effects working together, the GFA as has been thoroughly investigated earlier by Inoue et al [19].

Figure 4 shows M–H hysteresis loops of the as-cast Fe$_{72}$Y$_{6-x}$Nb$_x$B$_{22}$ and Fe$_{72}$Y$_{6-y}$Ta$_y$B$_{22}$ bulk glassy rods, 1 mm in diameter. The saturation magnetization slightly decreases from 1.47 T to 1.25 T or 1.32 T as Nb or Ta addition is 5 at% or 4 at%, respectively. The coercive force ($H_c$) is lower than 20 A m$^{-1}$ for all studied BMGs showing very good soft magnetic properties. The results depict that the addition of Nb or Ta into Fe–Y–B ternary BMG not only improves the GFA but also retains good soft magnetic properties.

The Curie temperature, $T_c$, as shown in Figure 5, gradually increases with the addition of Nb or Ta from 535 K ($x = 0$) to 563 K ($x = 5$) and 561 K ($y = 4$), respectively. The $T_c$ value depends on the magnetic interaction among Fe–Fe atoms. Our earlier researches revealed that the addition of Y manifestly decreases $T_c$ of ternary Fe–Y–B BMGs due to Ta replacement is 2–3 at% or 1–2 at%, respectively. The larger super-cooled liquid region reveals a higher resistance against crystallization. Included in Figure 3 are other GFA factors: reduced glass transition temperature, $T_{rg}$ ($= T_g / T_l$), and gamma factor, $T_x / (T_g + T_l)$ [20–22] to evaluate GFA criteria of the alloys. Yet both factors decrease with increasing Nb or Ta content and fail to describe the enormous enhancement in GFA. The reason for failure of these two factors comes from the almost invariant liquidus temperature of these alloys.

Typical M–H loops measured at room temperature are shown in Figure 4. The saturation magnetization slightly decreases from 1.47 T to 1.25 T or 1.32 T as Nb or Ta addition is 5 at% or 4 at%, respectively. The coercive force ($H_c$) is lower than 20 A m$^{-1}$ for all studied BMGs showing very good soft magnetic properties. The results depict that the addition of Nb or Ta into Fe–Y–B ternary BMG not only improves the GFA but also retains good soft magnetic properties.
the extremely large atomic size of Y which pulses apart the iron atoms, away from the optimal exchange interaction. This causes a decrement in exchange energy among them, hence a lower $T_c$ [11]. The partial replacement of Y by smaller-sized atoms, Nb or Ta, decreases the extent of pushing apart, so that the exchange interaction among them increases leading to a higher $T_c$.

The electrical resistivity linearly decreases with increasing Nb or Ta content from 230 to 190 $\mu\Omega$ cm. The extremely large Y atom in the amorphous matrix bestows a high strain at atomic level, leading to a high scattering effect of electron transport and thus an electrical resistivity higher than 200 $\mu\Omega$ cm in the glassy state [11]. The replacement of Y by Nb or Ta decreases the atomic strain and lowers the scattering effect so that electrical resistivity is lowered. However, the electrical resistivity is still much larger than that of conventional Fe–Si–B amorphous ribbons (∼140 $\mu\Omega$ cm).

Figure 6 shows the compressive test curves taken from 2 mm glassy rods of the Fe$_{72}$Y$_4$Nb$_2$B$_{22}$ and Fe$_{72}$Y$_4$Ta$_2$B$_{22}$ BMGs. Both of them almost fully elastic strain without plastic deformation before fracture and the fracture strain ($\varepsilon_f$) is 0.02. Both show extremely high compressive strength ($\sigma_f$) above 4000 MPa (4150 MPa and 4200 MPa) and high Young’s modulus (208 GPa and 210 GPa) for Nb- or Ta-modified BMGs, respectively. It almost reaches the maximum compressive strength available in the Fe-based BMGs developed to date, specifically, those with only four constituent elements and an Fe content higher than 70 at%.

The high compressive strength may result from the strong bonding nature of the constituent elements as is expected from the large negative heat of mixing mentioned above. The $T_c$ of these BMGs alloys is much higher compared with other Fe-based BMGs. It has been elucidated that $T_c$ highly correlates with the fracture strength and Young’s modulus such that the BMGs with higher $T_c$ exhibit better mechanical properties [23]. The BMGs in this study also support the correlation results between the $T_c$ and $E$. The micro-hardness monotonically increases with either Nb or Ta content from 990 (Nb, Ta = 0) to 1140 (Nb = 5) and 1200 (Ta = 4). The compressive strength, fracture strain and Young’s modulus for 2 at% Nb (Ta) modified BMGs are 4150 (4200) MPa, 0.02 (0.02) GPa and 208 (210) GPa, respectively. With a few at% Nb (Ta) and Y contents, these alloys show a combination of excellent GFA, good soft magnetic properties and high electrical resistivity and excellent mechanical strength. These BMG alloys thus have potential for future industrial applications.

4. Conclusions

The goal of improving GFA while retaining good soft magnetic properties of ternary Fe$_{72}$Y$_6$B$_{22}$ BMGs by partial substitution of Y with Nb or Ta was achieved in this study. The best GFA, shown by the capability to cast bulk glassy rods, was worked out as at least 4 mm for Fe$_{72}$Y$_{x}$Nb$_{y}$B$_{22}$ and at least 3 mm for Fe$_{72}$Y$_{x}$Ta$_{y}$B$_{22}$. The magnetic properties measured at room temperature showed that saturation magnetization decreases from 1.47 to 1.25 T with increasing Nb or Ta content. The coercivity of studied BMGs is less than 20 A m$^{-1}$. The Curie temperature increases from 535 to 563 K. The electrical resistivity is 230 to 190 $\mu\Omega$ cm. The micro-hardness monotonically increases with either Nb or Ta content from 990 (Nb, Ta = 0) to 1140 (Nb = 5) and 1200 (Ta = 4). The compressive strength, fracture strain and Young’s modulus for 2 at% Nb (Ta) modified BMGs are 4150 (4200) MPa, 0.02 (0.02) GPa and 208 (210) GPa, respectively. With a few at% Nb (Ta) and Y contents, these alloys show a combination of excellent GFA, good soft magnetic properties and high electrical resistivity and excellent mechanical strength. These BMG alloys thus have potential for future industrial applications.

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