Electronic-structure origin of the glass-forming ability and magnetic properties in Fe–RE–B–Nb bulk metallic glasses


Abstract

(Fe_{0.71}RE_{0.09}B_{0.24}Nb_{0.09}) bulk metallic glasses (BMGs) were found exhibiting excellent glass-forming ability (GFA) with critical diameters ranging from 3.5 to 6.5 mm, and high compressive fracture strength larger than 4300 MPa. Moreover, they displayed good soft-magnetic properties with saturation magnetic flux density of 0.71–0.87 T, coercive force of 1.23–39.76 A/m and effective permeability of 1500–12,740 at 1 kHz. X-ray photoelectron spectroscopy was performed to clarify the origin of the excellent GFA from the viewpoint of electronic structure. It was found that the Tm doped alloy displayed unique electronic structure including the deepest core-level binding energy, the most numerous RE–B bonds and the minimum density of states near the Fermi level, making this alloy the best glass former. The various trends noticed in the magnetic properties were ascribed mainly to the differences in the magnetic anisotropy and magnetic moment of RE elements.

1. Introduction

Fe-based metallic glasses have been widely used in electrical devices such as core materials of distribution transformers and reactors, due to their appealing combination of low materials cost, excellent soft-magnetic properties and high corrosion resistance. Unfortunately, most of the Fe-based metallic glasses were limited to thin ribbons with thickness less than 50 μm, since the critical cooling rate required to hinder crystallization in these metallic glasses was about the order of 10^5–10^6 K/s [1]. Accordingly, the synthesis of Fe-based bulk metallic glasses (BMGs) with high glass-forming ability (GFA) has become a subject of considerable scientific interest [2–10]. Lin et al. reported that minor addition of rare earth (RE) elements (Sc, Y, Dy, Ho, and Er) was an effective approach to improve the GFA of Fe–B binary alloys without significantly deteriorating the soft-magnetic properties [7]. However, the critical dimension of these BMGs is no more than 2 mm. Recently, BMGs with a critical diameter of 5.5 mm were obtained in the quaternary (Fe_{0.71}Dy_{0.09}B_{0.24}Nb_{0.09}) alloy system, which also exhibited good soft-magnetic and mechanical properties [11]. The reasons for the enhanced GFA with minor addition of Dy element were attributed to: (a) the large negative mixing enthalpies and atomic-size mismatch among the component elements; (b) the decrease of liquidus temperature; and (c) the competitive formation process of the complex Fe_{2}B_{6} and Dy_{2}Fe_{14}B phases. However, the structural origin of the high GFA in these alloys has not yet been well understood.

Recently, X-ray photoelectron spectroscopy (XPS) has been a popular tool for characterizing the electronic structure and the corresponding local atomic environment of metallic glasses [12–16]. The electronic structure is related to the chemical bonding of an atom to its close neighbors, and the variation of the bond order through the band can be obtained [17]. Buttner et al., corroborated through XPS the impact of the addition of Er on the local atomic structure and hence the electronic structure in Fe-based bulk metallic glasses [16]. Moreover, some studies have shown the relationship between the electronic structure and the glass forming ability. Alamgir et al. [18] obtained the XPS spectrum of Pd–Ni–P BMGs and found that at one particular composition the electronic structure changes as a result of the transition from a glassy to a crystalline state. This small difference in electronic structure between the glass and the crystalline state could be a reason for the high glass stability at this composition.

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Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China
School of Mechanics and Civil Engineering, China University of Mining and Technology, Xuzhou 221116, China
Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
measured the photoemission spectra of Pd–Ni–Cu–P and Pd–Ni–P BMGs and found that the Pd 4d partial density of states (DOS) near the Fermi energy largely decreases which may potentially be related to the excellent glass-forming ability of these BMGs. Generally, magnetic heavy RE elements (the number of 4f electron is more than 6) have a localized magnetic moment, which significantly affect the electronic structure of the examined alloy. For this reason the metallic glasses containing heavy RE and Fe elements show various interesting magnetic properties [9,20–22]. Therefore, in this paper, we have investigated the influence of the addition of RE on GFA of (Fe0.71RE0.05B0.24)96Nb4 (RE = Gd, Tb, Ho, Er, Tm) BMGs, and studied the electronic structure using X-ray photoelectron spectroscopy to find the underlying mechanism involved in the improvement of GFA. We also present in detail the results and origin of magnetic and mechanical properties of these heavy RE doped Fe-based BMGs.

2. Experiment

Master ingots with nominal compositions of (Fe0.71RE0.05B0.24)96Nb4 (RE = Gd, Tb, Ho, Er, Tm) were prepared by arc melting the mixtures of high-purity elements (Fe: 99.95 wt.%, Gd: 99.95 wt.%, Tb: 99.95 wt.%, Ho: 99.95 wt.%, Er: 99.95 wt.%, Tm: 99.95 wt.%, B: 99.95 wt.%, Nb: 99.99 wt.%) purity) under an argon atmosphere. The ingots were re-melted at least four times in order to achieve a good chemical homogeneity of the entire master ingots. Metallic glass ribbons with a cross-section of 1–1.5 × 0.025–0.035 mm² were prepared by single roller melt-spinning method in an argon atmosphere with a surface speed of ~36 m/s. Additionally, pieces of each ingot were re-melted in quartz tubes and then cylindrical rods with diameters up to 6.5 mm were prepared by copper mold casting. The amorphous and crystallized structures of cylindrical rods were identified by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation. The glass transition and crystallization behavior of the as-quenched samples were examined by differential scanning calorimeter (DSC, NETZSCH 404C) under a heating rate of 0.667 K/s, and the solidification behavior of the as-quenched ribbons were examined by differential scanning calorimeter (DSC, NETZSCH 404C) under a heating rate of 0.667 K/s. The possible reason for the smallest ΔTg value of 68 K, it also had the largest Tg value of 0.622 K. Apparently, Tg principle was more suitable than ΔTg, for predicting the best GFA in the present alloy system. Another interesting feature of the DSC traces is the abnormal exothermic peak (labeled Tc) in the SCLR, which has been considered to originate from the formation of local chemical short-range order during heating [25–27]. The possible reason for the smallest ΔTg of the alloy containing Tb may be related to the absence of the Tc in the SCLR. BMGs with such unusual exothermic peaks always have larger ΔTg compared with the other alloys in the same alloy system [9,25–29]. The detailed studies of the relationship between ΔTg and Tc are worthy of more investigation.

In order to further understand the mechanism of effect of RE elements addition on GFA, we investigated the electronic structure of both, the excellent glass-former, (Fe0.71Tm0.05B0.24)96Nb4, and the relatively poor glass-formers, (Fe0.71Gd0.05B0.24)96Nb4 and (Fe0.71Tb0.05B0.24)96Nb4. The Fe 2p and B 1s core level spectra obtained from the (Fe0.71RE0.05B0.24)96Nb4 (RE = Gd, Tb, Tm) BMGs, are shown in Fig. 3(a) and (b). For comparison purposes the spectra in each plot have been shifted up or down as necessary. The Fe 2p spectra showed the spin–orbit-split 2p1/2 and 2p3/2 Components, separated by about 14 eV. The main peak positions of Fe 2p3/2 changed gradually to lower binding energies as increasing the atomic number of RE element (inset Fig. 3(a)). The fitting of Fe 2p3/2 curve were performed by using the vision processing software, Kratos Vision (Kratos Analytical Ltd.) from where an accurate assessment of the Fe2p peaks could be made. The peak shifted from 706.96 eV for RE = Gd to 706. 82 eV for RE = Tm, i.e. the core-level binding energy of the Tm-doped alloy was 0.14 eV smaller than that of the other alloys. However, there was no significant change in binding energy for the peaks of B 1s (Fig 3b inset) and Nb 3d (not shown here).

Fig. 3(c) displays the variation of the valence band structure of (Fe0.71RE0.05B0.24)96Nb4 resulting from different RE elements addition. The spectra are normalized to the same height at their maximum peaks and moved up and down as necessary. For comparison, the XPS spectrum of Fe reproduced from reference [30] is shown in the inset, which exhibits a characteristic hump at lower energy side associated with Fe 3d band. When alloying elements were added, the valence band between 0 and 6 eV was dominated strongly by contributions from Nb and Nb and Fe 3d-bands. The main difference in the spectra from that of pure Fe was an additional binding energy region between 6 and 10 eV due to the presence of overlapped B 2s and RE 4f states. The 4f electron photoemission often overlaps photoemission from the host valence band [31].

![Fig. 1. XRD patterns of the (Fe0.71RE0.05B0.24)96Nb4 (RE = Gd, Tb, Ho, Er, Tm) BMGs with critical diameters varying from 3.5 to 6.5 mm.](Image)
broad B 1s and RE 4f spectrum for the alloy containing Tb was decomposed into two peaks with the addition of Tm, suggesting a localized nature of these electrons when the atomic number of the RE increases. Additionally, the d band was clearly distorted. It has been shown that the XPS valence band spectrum closely resemble the total valence band density of states [32,33]. We can

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$D_{\text{max}}$</th>
<th>$\phi$ (mm)</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$A_T$ (K)</th>
<th>$T_{\text{rel}}$ (K)</th>
<th>$B_r$ (T)</th>
<th>$H_c$ (Am$^{-1}$)</th>
<th>$\mu_r$ (1 kHz)</th>
<th>$\sigma_r$ (MPa)</th>
<th>$H_v$ (kg/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Fe$<em>{0.71}$Gd$</em>{0.05}$B$<em>{0.24}$)$</em>{96}$Nb$_4$</td>
<td>3.5</td>
<td>865</td>
<td>982</td>
<td>117</td>
<td>1485</td>
<td>0.582</td>
<td>0.76</td>
<td>3.86</td>
<td>10,090</td>
<td>4300</td>
<td>1100</td>
</tr>
<tr>
<td>(Fe$<em>{0.71}$Tb$</em>{0.05}$B$<em>{0.24}$)$</em>{96}$Nb$_4$</td>
<td>3.5</td>
<td>863</td>
<td>991</td>
<td>128</td>
<td>1474</td>
<td>0.585</td>
<td>0.71</td>
<td>39.76</td>
<td>1500</td>
<td>4260</td>
<td>1090</td>
</tr>
<tr>
<td>(Fe$<em>{0.71}$Ho$</em>{0.05}$B$<em>{0.24}$)$</em>{96}$Nb$_4$</td>
<td>5</td>
<td>866</td>
<td>967</td>
<td>101</td>
<td>1467</td>
<td>0.590</td>
<td>0.75</td>
<td>3.97</td>
<td>10,680</td>
<td>4310</td>
<td>1110</td>
</tr>
<tr>
<td>(Fe$<em>{0.71}$Er$</em>{0.05}$B$<em>{0.24}$)$</em>{96}$Nb$_4$</td>
<td>5.5</td>
<td>868</td>
<td>964</td>
<td>96</td>
<td>1463</td>
<td>0.593</td>
<td>0.74</td>
<td>3.54</td>
<td>10,810</td>
<td>4330</td>
<td>1110</td>
</tr>
<tr>
<td>(Fe$<em>{0.71}$Tm$</em>{0.05}$B$<em>{0.24}$)$</em>{96}$Nb$_4$</td>
<td>6.5</td>
<td>868</td>
<td>936</td>
<td>68</td>
<td>1396</td>
<td>0.622</td>
<td>0.87</td>
<td>1.23</td>
<td>12,740</td>
<td>4390</td>
<td>1120</td>
</tr>
</tbody>
</table>

Fig. 2. DSC curves of the (Fe$_{0.71}$RE$_{0.05}$B$_{0.24}$)$_{96}$Nb$_4$ (RE = Gd, Tb, Ho, Er, Tm) alloys: (a) glass transition and crystallization behavior measured at heating rate of 0.667 K/s and (b) solidification behavior investigated at cooling rate of 0.067 K/s.

Fig. 3. XPS spectra of the (Fe$_{0.71}$RE$_{0.05}$B$_{0.24}$)$_{96}$Nb$_4$ (RE = Gd, Tb, Tm) glassy alloys: (a) core-level spectra of Fe 2p, (b) core-level spectra of B 1s, (c) valence band spectra and (d) magnified valence band spectra near the Fermi energy. The inset of figure (c) is the XPS spectrum of Fe reproduced from reference [31].
infer from the valence band spectra of RE = Tm that the total number of valence electrons increase and hence the probability of forming RE–B bonds is higher. The increase in charge density induced by reduced interatomic distance will enhance the shielding effect on the core electrons, thereby resulting in a smaller core-level binding energy [34,35]. From the core-level spectra it is seen that the lowest binding energy corresponds to RE = Tm, as a result, the addition of Tm is expected to introduce the shortest interatomic distance and thus improve the atomic packing efficiency. Based on the Miracle’s structure model [36], the atomic packing efficiency is favorable for glass formation; this could explain the higher GFA obtained when adding Tm. Additionally, it has been reported that the metal–metalloid bonds not only destabilize the competing crystalline phases, but also stabilize the liquid phase, which is beneficial for the enhancement of GFA [37]. Although the relative variations of the binding energies are about 0.1 eV, the small change in the electronic structure can remarkably affect the GFA of the alloys. This was observed in Fe–Co–Cr–Mo–B–C–Y BMGs, where even a shift of 0.1 in the core-level binding energy noticeable increased the GFA from 3 to 12 mm [34].

The relationship between electronic structure and GFA can also be understood using the nearly free-electron model. According to the nearly-free-electron model, the alloy with the best GFA corresponds to the one for which the density of states near the Fermi level, N(Ef), lies at a minimum [38]. An enlarged view of N(Ef) of the original normalized valence spectra is presented in Fig. 3(a). As shown, the Tm doped alloy exhibited the lowest N(Ef), while the alloys containing Gd and Tb displayed the same behavior. These observations are consistent with the trend of GFA. Thereby, the excellent GFA of the Tm doped alloy is closely correlated to the deepest core-level binding energy, the most numerous RE–B bonds, and lowest N(Ef) compared to the other alloys.

The σf (as shown in Table 1) can be also interpreted from the viewpoint of bonding nature. The addition of RE element effectively promoted the formation of highly dense packed structure [39], thus leading the achievement of super high fracture strength of about 4300 MPa. Accordingly, it is logical to suppose that the Tm doped alloy exhibited the highest σf (4390 MPa) mainly due to the densest packing structure and the most numerous RE–B bonds existing in this alloy.

Fig. 4 represents the variations of (a) Hc, (b) μe, and (c) Bs as a function of RE elements in the (Fe0.71RE0.05B0.24)96Nb4 (RE = Gd, Tb, Ho, Er, Tm) BMGs. All the samples for magnetic property measurements were annealed at temperatures of Tg ~ 50 K for 600 s in order to release residual stress. XRD analysis was performed to monitor the amorphous structure. The XRD results (not shown here) showed that the examined samples had fully amorphous structure without any crystallization. The values of Hc, μe, and Bs are also listed in Table 1. As shown in Fig. 4 and Table 1, the alloy containing Tb exhibited the maximum Hc value of 39.76 A/m, while the Hc values of the rest alloys were less than 4 A/m. As expected, μe exhibited an opposite trend. The alloy with Tb addition displayed the minimum μe value of 1500, whereas the μe values of the other alloys were more than 10,000. Meanwhile, the highest value of Bs (0.87 T) was observed for the RE = Tm alloy and the lowest (0.71 T) for the RE = Tb alloy, but almost no difference in Bs was detected for the alloys doped with Gd, Ho, and Er (0.74–0.76 T). We therefore conclude that the (Fe0.71Tm0.05B0.24)96Nb4 BMG exhibits the best overall performance in the Fe–RE–B–Nb alloy system, i.e., highest GFA of 6.5 mm, largest Bs of 0.87 T, maximum μe of 12,740, and lowest Hc of 1.23 A/m.

It is reasonable to suppose that the variations of Hc for the whole set of alloys are ascribed mainly to the addition of RE elements, which exhibit different magnetic anisotropy constants. If we assume that the magnetization reversal takes place by domain wall motion, the Hc can be described by [40,41]:

\[
H_c \approx 2K/(\mu_0 M_s) + \beta(\sqrt{2}r/\mu_0 M_s)^2
\]  

(1)

where K is the magnetic anisotropy constant, μ0 is the vacuum permeability, M_s is the saturation magnetization, βσ is proportional to the magnetic anisotropy constant, and α and β are constants.

It is obvious that the trends of Hc and magnetic anisotropy are consistent, thus the magnetic anisotropy characteristics of RE elements significantly affect the Hc. The huge anisotropy in Tb–Fe amorphous alloys caused by the unique 4f electronic cloud of Tb (oblate ellipsoid structure with magnetic moment perpendicular to the equatorial plane) [42], generates a particular magnetic behavior in Fe–B–Nb–RE system. Thereby, the alloy with addition of Tb possesses the highest Hc value of 39.76 A/m. On the contrary, the alloy containing Tm shows the smallest magnetic anisotropy because the exchange energy of Tb–Fe is lower than those of (Gd, Tb, Ho, Er)–Fe [43], leading to the lowest Hc value of 1.23 A/m. Since Gd has no orbital angular momentum (L = 0), the Fe–Gd alloys usually have a weak magnetic anisotropy. Besides, Ho and Er also exhibit a very low magnetic anisotropy compared with Tb [44]. Therefore, these three alloys show low Hc values of about 4 A/m. A totally opposite trend is observed for the variation of μe, which is a common phenomenon in amorphous and nanocrystalline alloys.

It is also for this reason that different RE alloying elements may have different effects on the Bs of Fe–RE–B–Nb alloys, as shown in Eq. (1). The variation of Bs can also be understood on the basis of the magnetic moment values of RE elements. Usually RE (4f) exhibits antiferromagnetic coupling with Fe (3d), thus the larger the magnetic moment of RE element, the smaller the Bs of alloy. The magnetic moments of Gd, Tb, Ho, Er, and Tm are 7.55, 9.34, 10.34, 8, and 3.4 μB, respectively [44]. It is expected that the Ho-containing alloy should show the lowest Bs, but the obtained data are not consistent with the expectation. In order to understand the origin of this discrepancy, the temperature dependence of magnetic moments of the (Fe0.71RE0.05B0.24)96Nb4 (RE = Tm, Ho, Tb) BMGs under an applied field of 1 T was investigated, as illustrated in Fig. 5. Clearly, the magnetic moment of the RE = Tm alloy remained the largest over the entire temperature range, so its Bs was the highest. The magnetic moments of RE = Tm and Ho alloys
increased with increasing temperature within a certain temperature range, due to their large positive thermal coefficient of $B_s$. Specifically, the largest thermal coefficient at room temperature occurred in the RE = Ho alloy, whereas nearly zero in the RE = Tb alloy. This is because the Ho–Fe interaction is weaker than the Tb–Fe interaction upon the heating process [45]. Therefore, the RE = Ho alloy exhibited larger magnetic moment than the RE = Tb alloy at room temperature. That is why the $B_s$ of RE = Ho alloy is larger than the one of RE = Tb alloy.

4. Conclusions

The effects of heavy RE elements addition on the GFA, magnetic and mechanical properties of (Fe$_{0.71}$RE$_{0.05}$B$_{0.24}$)$_{96}$Nb$_4$ (RE = Gd, Tb, Ho, Er, Tm) BMGs were investigated. BMG rods with critical diameters ranging from 3.5 to 6.5 mm were developed by copper mold casting. In addition to the high GFA, the glassy alloys exhibited good soft-magnetic and mechanical properties, i.e., high saturation magnetic flux density and low coercive force ranging from 0.71 to 0.87 T and 1.23–39.76 A/m, respectively, and high fracture strength and Vickers hardness of 4260–4390 MPa and 1090–1120 kg/mm$^2$, respectively. The electronic structure of the alloy system was examined in order to clarify the origin of the variation trends of GFA and magnetic properties. In particular, the addition of Tm introduced the lowest core-level binding energy, the most numerous RE–B bonds and the minimum density of states near the Fermi level, which may be closely related to the best GFA of the (Fe$_{0.71}$Tm$_{0.05}$B$_{0.24}$)$_{96}$Nb$_4$ BMG. Furthermore, the smallest magnetic anisotropy and largest magnetic moment of the alloy confers it the excellent soft-magnetic properties.

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References