Soft magnetic ternary iron-boron-based bulk metallic glasses

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Ternary iron-boron-based bulk metallic glasses (BMGs) were explored exhibiting capability of thick amorphous casting at least 1 mm in rod diameter or 0.5 mm in plate thickness, excellent soft magnetic properties with saturation magnetization 1.56 T and coercivity smaller than 40 A/m, and electrical resistivity larger than 200 μΩ cm. The BMG alloys represented by the formulas $M_1\text{Fe}_2\text{B}_c$, are based on two simple selection rules: (1) $M$ is an element with an atomic radius at least 130% that of Fe; (2) $M$ possesses eutectic points with both Fe and B, and the M-Fe eutectic is at the Fe-rich end. Among more than 30 candidate $M$ elements, Sc, Y, Dy, Ho, and Er fulfill BMG capability at the composition range, in at %, $3 < a < 10$, $18 < c < 27$, whereas $a + b + c = 100$. It is very remarkable that with a tiny addition of $M$, such as 4 at %, the critical cooling rate to form an amorphous state is abruptly lowered by more than four orders of magnitude as compared with Fe-B binary alloys, and a bulk amorphous state is achievable with only three elements (conventional ones 4–7 elements). These alloys are promising as core materials for transformers. © 2005 American Institute of Physics. [DOI: 10.1063/1.1901808]

Since the preparation of amorphous Fe-P-C thin foils in 1967 by a rapid solidification technique, a large number of iron-based amorphous metals have been subsequently developed. It is well known that such alloys are very attractive because of their excellent soft magnetic properties. These materials have been widely used in electronic devices such as transformer cores. If all the core materials of transformers and motors will be made of iron-based amorphous metals, the impact on energy saving and reduction in CO₂, thus end. Among more than 30 candidate $M$ elements, Sc, Y, Dy, Ho, and Er fulfill BMG capability at the composition range, in at %, $3 < a < 10$, $18 < c < 27$, whereas $a + b + c = 100$. It is very remarkable that with a tiny addition of $M$, such as 4 at %, the critical cooling rate to form an amorphous state is abruptly lowered by more than four orders of magnitude as compared with Fe-B binary alloys, and a bulk amorphous state is achievable with only three elements (conventional ones 4–7 elements). These alloys are promising as core materials for transformers. © 2005 American Institute of Physics.

FIG. 1. X-ray diffractograms taken on cross sections of as-cast rods 1 and 2 mm in diameter of an $Y_6\text{Fe}_{72}\text{B}_{22}$ alloy, Cu $K\alpha_1$. 

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prepared by arc melting in a copper crucible mixtures of prealloyed Fe-B ingots, beads of pure M metal of at least 99.5% purity, under a vacuum 0.01 MPa. Glassy ribbons with a cross section of about $0.03 \times 3 \text{ mm}^2$ were prepared by a single-roller melt-spinning technique. Rods or plates with different diameters or thicknesses were prepared by injection casting into a copper mold. The structure of ribbons and as-cast rods/plates was examined by x-ray diffractometry (XRD). Thermal stability was studied by differential scanning calorimetry (DSC) at a heating rate of 20 K/min. Magnetic properties, including saturation magnetization ($I_s$) and coercive force ($H_c$), were measured with a vibrating sample magnetometer (VSM). Curie temperature ($T_c$) was measured by a thermal-gravimetric analyzer under a magnetic field of 0.02 T ($M$-TGA) at a heating rate of 5 K/min.

First of all, the elements selected using the above two rules were examined. Table I summarizes the as-cast results of some of the selected elements. We can see that scandium (Sc), yttrium (Y), dysprosium (Dy), holmium (Ho), and erbium (Er) exhibited good glass forming ability in forming glassy rods of at least 1 mm in diameter, or plates at least 0.5-mm thick. According to the results, one can see that the alloys with M being one of zirconium, hafnium, niobium, or tantalum, whose atomic size is smaller than 130% that of Fe, failed to form BMG, though they possess eutectic points with Fe and B. Those elements possessing no Fe-rich eutectic point with Fe, such as lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, and terbium, also failed to form BMGs, even though they have an atomic size much larger than 130% that of Fe. Only elements such as Sc, Y, Dy, Ho, and Er that simultaneously satisfy our two proposed rules, exhibited good GFA to form ternary bulk metallic glasses. The experimental results prove the validity of our proposal for the selection of simple ternary Fe-based bulk glassy alloys.

Second of all, further GFA tests showed that the alloys Sc$_6$Fe$_{72}$B$_{22}$, Y$_6$Fe$_{72}$B$_{22}$, and Er$_6$Fe$_{72}$B$_{22}$ exhibit excellent GFA to form glassy rods with a diameter of at least 2 mm. Figure 1 depicts the x-ray diffraction patterns taken from the transverse cross sections of as-cast rods of Y$_6$Fe$_{72}$B$_{22}$ with 1 and 2 mm diam, respectively, showing an amorphous structure. DSC studies revealed that the Sc-added alloy possessed much lower $T_s$ and $T_x$ than others. The $\Delta T_s$ ($T_x - T_s$) became the largest (42 K) as M is yttrium, and the smallest (16 K) as M is erbium.

We then varied the amount of yttrium addition to test the composition range for BMGs. Figure 2 shows the composition region for the formation of at least 1-mm-diam bulk glassy rod in the Fe-Y-B ternary alloy. For corresponding plate casting, the achievable thickness is 0.5 mm. It shows a very wide bulk glassy formation range as $3 < Y < 10$ at % and $18 < B < 27$ at %. Other systems of Fe-M-B alloys ($M$ = Sc, Dy, Ho, Er) also exhibited a similar, wide BMG forming region around the composition of M$_6$Fe$_{72}$B$_{22}$. For example, 2-mm glassy rods were successfully achieved in Sc$_6$Fe$_{72}$B$_{22}$, Y$_6$Fe$_{72}$B$_{22}$, and Er$_6$Fe$_{72}$B$_{22}$.

It is well known that the binary Fe-B system exhibit poor glass forming ability to form a glassy ribbon around 30 $\mu$m in thickness only by a rapid solidification technique, such as melt spinning, corresponding to a cooling rate of $10^6$ K/s. It was indeed very astonishing that with a tiny amount of M addition, such as 4 – 6 at % Sc, Y, Dy, Ho, and Er, the critical cooling rate ($R_c$) to form an amorphous state is at least four orders of magnitude lower. A bulk glassy state is possible through an injection casting into a copper mold that has a cooling rate only of $10 – 10^2$ K/s. On the other hand, it has long been recognized that Fe-based BMGs are quite difficult to achieve through simple compositions. They were known to be achievable for alloys with more than three elements, and in practice only for alloys containing 4–7 elements. We believe that the proper packing of an extremely large atom (such as Sc, or Y) with its eutectic (negative-heat-of-mixing) and medium-sized counterpart, iron, and the extremely small atom, boron, has led to a topological effect that hinders one another from crystallization. This will then open a door to attain simple BMGs other than Fe-based alloys.
TABLE II. A comparison of saturation magnetization \((I_s)\) for various Fe-based BMGs.

<table>
<thead>
<tr>
<th>BMG alloy systems</th>
<th>(I_s) (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>(Y_2Fe_{23}B_{20}) 1.56</td>
</tr>
<tr>
<td></td>
<td>(M_2Fe_{23}B_{22}) ((M=Sc/Dy/Ho/Er)) 1.2–1.3</td>
</tr>
<tr>
<td>Fe-B-Si ribbon</td>
<td>(Fe_{80}B_{11}Si_9) 1.59</td>
</tr>
<tr>
<td>Known Fe-based BMGs</td>
<td>((Fe,Co,Ni)-(Zr,Nb,Hf)B) 1.0</td>
</tr>
<tr>
<td></td>
<td>(Fe-Al-Ga-P(Si,B)) 1.3</td>
</tr>
<tr>
<td></td>
<td>(Fe-Co-Ln-B) 1.37</td>
</tr>
<tr>
<td></td>
<td>(Fe-Nb-Si-B); Fe-Zr-Si-B (&gt;1.5)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 2.  
\(^b\)Reference 7–9.  
\(^c\)Reference 3–6.  
\(^d\)Reference 14.  
\(^e\)Reference 12.  
\(^f\)Reference 13.

The Curie temperature \((T_c)\), measured by a thermogravimetry analyzer coupled with a magnetic field \((M-TGA)\), decreases from 568 to 487 K as Y and B increases from 4 to 8 and 22 to 26 at %, respectively. Figure 3 shows the variation in saturation magnetization \((I_s)\) of the \(M\)-Fe-B bulk glassy alloys. The results show that the \(Y_2Fe_{78}B_{22}\) BMGs exhibit much higher \(I_s\) than other \(M_2Fe_{78}B_{22}\) ternary BMGs under study, and attain the highest \(I_s\) at the Y content of 4–6 at %, up to 1.52 T. For a BMG of \(Y_2Fe_{78}B_{22}\) an \(I_s\) of 1.56 T was attained, which is higher than those of reported multicomponent Fe-based BMGs and comparable with \(Fe_{80}B_{11}Si_9\) amorphous ribbon, as can be seen in Table II. Yttrium has no magnetic moment at all, so that it plays a simple role of diluting the magnetic moment, whereas Dy, Ho, and Er are heavy rare earths that are antiferromagnetically coupled with Fe in Fe-Sc binary amorphous alloys. We propose that Sc behaves the same way in amorphous ternary Sc-Fe-B alloys resulting in a lowered saturation magnetization. The coercive force \((H_c)\) of all the as-cast ternary BMGs was smaller than 40 A/m, with the smallest being 4 A/m for \(Y_2Fe_{78}B_{22}\). The electrical resistivity of the \(M\)-Fe-B glassy alloys measured by a four-point-probe method from melt-spin ribbons for each composition is typically 200–290 \(\mu\Omega\) cm and increasing with \(M\) and B contents. This is almost two times that of the conventional amorphous \(Fe_{79}Si_3B_{13}\) ribbon (around 140 \(\mu\Omega\) cm) and five times that of silicon steels (around 50 \(\mu\Omega\) cm). The reason is very simple that the extremely large difference in atomic size among \(M\), Fe, and B induces, at the atomic scale, enormous lattice strain that contributes to extra electronic scattering during electrical transport.

In summary, simple rules of composition selection for Fe-B-based ternary bulk glassy alloys, \(M\)-Fe-B, were established by modifying the previous empirical rules: (1) \(M\) is an element with an atomic radius at least 130% that of Fe; (2) \(M\) possesses eutectic points with both Fe and B, and the \(M\)-Fe eutectic is at the Fe-rich end. This led to an excellent outcome, whereby the addition of a tiny amount of \(M\), such as 4–6%, with \(M\) being one of Sc, Y, Dy, Ho, or Er, the critical cooling rate to form an amorphous state is abruptly lowered by more than four orders of magnitude as compared with the Fe-B binary alloys. It is also surprising that for a long time, Fe-based BMGs were recognized to be achievable for alloys containing more than three elements, and in practice 4–7 elements. The ternary BMGs thus developed are characteristic of high saturation magnetization 1.2–1.56 T, low coercivity less than 40 A/m, and high electrical resistivity, larger than 200 \(\mu\Omega\) cm. Among the explored ternary BMGs, Y-Fe-B alloys show the highest saturation magnetization, 1.56 T, and display great potential for application due to the cheap and relatively abundant yttrium, besides their promising magnetic properties. Also, the magnetic interaction between Sc, Y, Dy, Ho, Er, and the amorphous Fe-B matrix is worthy of further investigation.

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