Magnetic properties and glass-forming ability of modified Fe–P–Si–B bulk amorphous alloys

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Abstract

Thermal and magnetic properties of Al, Sn and C modified Fe–P–Si–B amorphous alloys with compositions Fe\textsubscript{80−x−y−z}Al\textsubscript{x}Sn\textsubscript{y}P\textsubscript{12−z}Si\textsubscript{4}B\textsubscript{4}C\textsubscript{z} (in at\%, x = 3−5, y = 1−7, z = 0−6) were investigated. By suitable replacements of Fe by Al/Sn, and P by C in these alloys, the glass-forming ability is greatly enhanced. The super-cooled liquid region and reduced glass transition temperature were examined and compared to the modified alloys. Properties of Fe\textsubscript{74}Al\textsubscript{4}Sn\textsubscript{2}P\textsubscript{12}Si\textsubscript{4}B\textsubscript{4}C\textsubscript{z} amorphous alloys are typically, with increasing z: saturation magnetization 1.28−1.38 T, coercive force around 40 A/m, Curie temperature of 547−595 K, the electrical resistivity decreases from 181 to 168 $\mu$Ω·cm. Magnetic inductance of the cast cores were also reported.

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1. Introduction

Since the first amorphous alloy Au–Si was synthesized in 1960, amorphous alloys have attracted much attention due to many unique properties comparing with their crystalline counterparts. Many amorphous alloy systems were developed and various industrial applications were also established. Ever since the first Fe-based amorphous Fe–P–C alloy was discovered in 1967, a lot of Fe-based amorphous alloy systems have been developed, such as (Fe,Co)–Si–B in 1974, followed by (Fe,Co,Ni)–(Cr,Mo,W)–C, (Fe,Co,Ni)–(Zr,Hf) and then (Fe,Co,Ni)–(Zr,Hf,Nb)–B amorphous alloy systems [1]. The Fe-based amorphous alloys are very attractive due to their conspicuous soft magnetic properties and have become most important in industrial usages among all the

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amorphous alloys. The (Fe,Co)–Si–B amorphous alloys have been widely used in transformers, sensors, among others. However, there are serious disadvantages of these alloys that high cooling rates above \(10^5\) K/s are required to achieve amorphous state due to their low glass-forming ability (GFA), so that the alloy thickness was limited below 50 \(\mu\)m [2]. This in turn greatly limits applicability. Thicker ferromagnetic amorphous alloys, better in bulk forms, have been urgently desired. Great efforts have been made to improve the GFA of Fe-based alloys.

Recently a large number of bulk glassy alloys were explored in multi-component Mg-, Ln- (Ln=lanthanide metals), Zr- and Zr–Ti-based alloy systems. These bulk amorphous metals exhibit wide super-cooled liquid region above 60 K before crystallization, leading to better resistance to crystallization [3–8]. These alloys with better GFA satisfy the following three empirical rules: (1) multi-component alloys consist of more than three, usually 5–6 elements; (2) larger difference in atomic size is better, necessarily larger than 12%; and (3) large negative heat of mixing. Since 1995, new Fe-based amorphous alloys with wide super-cooled liquid region were developed according to the above empirical rules. They are Fe–(Al,Ga)–(P,C,B,Sn)–B [9–12]; (Fe,Co,Ni)–(Zr,Hf,Nb)–B [13–15]; Fe–Co–Ln–B alloys [16]. Among the Fe–P–Si–B alloys, the Fe\(_{80}\)P\(_{12}\)Si\(_4\)B\(_4\) composition was found to have the best of all GFA [9].

There are two important factors for the evaluation of GFA: (1) as large as possible super-cooled liquid region (\(\Delta T_x\)) defined by the difference between crystallization temperature (\(T_x\)) and glass transition temperature (\(T_g\)), (2) the higher the better reduced glass transition temperature, \(T_{rg} = T_g/T_m\) (\(T_m\) is the melting temperature).

This study was intended to investigate the effect of Sn, Al and C additions into the Fe\(_{80}\)P\(_{12}\)Si\(_4\)B\(_4\) alloy on the GFA, thermal properties and soft magnetic properties.

2. Experimental

Multi-component alloy ingots with nominal compositions Fe\(_{80-x-y}\)Al\(_{x}\)Sn\(_y\)P\(_{12-z}\)Si\(_4\)B\(_4\)C\(_z\) (in at\%,

\(x = 0–5, \ y = 0–7, \ z = 1–6\) were prepared by induction melting the mixtures of pure iron, pre-alloyed Fe–P, Fe–B, Fe–C ingots, pure Si, Sn and Al metals under a vacuum \(10^{-1}\) atm. Ribbons with a cross section of about \(0.03 \times 10\) mm\(^2\) were prepared by a single-roller melt-spinning technique. Bulk samples in rod form with different diameters were prepared by a copper mold injection casting method. The structure of ribbons and cast rods were examined by X-ray diffractometry. The thermal properties associated with glass transition temperature (\(T_g\)), crystallization temperature (\(T_x\)) and super-cooled liquid region (\(\Delta T_x = T_x - T_g\)) were studied by differential scanning calorimetry (DSC) at a heating rate \(0.67\) K/s. The melting point (\(T_m\)) was measured by differential thermal analysis (DTA). Magnetic properties including saturation magnetization (\(I_c\)) and coercive force (\(H_c\)) were measured with a vibrating sample magnetometer (VSM). Permeability and magnetic inductance were measured with an impedance analyzer. Curie temperature (\(T_c\)) was measured by a magnetic-thermal-gravimetric analyzer (M-TGA) at a heating rate \(5\) K/min. Core loss was measured at a frequency of \(50\) Hz under different external magnetic fields, typically from 0.5 to 1.1 T by using an alternating current magnetic measurement. The electrical resistivity was measured by a typical four-point probe method with necessary calibrations. Hardness of bulk glassy samples was measured by the micro Vickers method.

3. Results and discussion

3.1. Structure and thermal properties

The studies on the effect of replacing Fe by Sn in Fe\(_{80-x-y}\)Sn\(_y\)P\(_{12}\)Si\(_4\)B\(_4\) (\(y = 1–6\) at\%) alloys on the super-cooled liquid region, \(\Delta T_x\) showed that the \(\Delta T_x\) increases from 36 as \(y = 0\) to the maximum value of 46.5 as \(y = 6\) at\% [17]. These alloys also exhibit good soft magnetic properties. With increasing \(y\), the saturation magnetization (\(I_c\)) decreases gradually from 1.33 to 1.11 T; the coercive force (\(H_c\)) gradually increases from 2.86 to 7.86 A/m and the maximum permeability (\(\mu_m\))
lies between 134,000 ($y = 1$) and 49,000 ($y = 6$). However, these alloys are not able to cast into bulk glassy rods of 1 mm in diameter.

By fixing $y = 2$, Al was further added into the Fe$_{78-x}$Al$_x$Sn$_2$P$_{12}$Si$_4$B$_4$ ($x = 3-5$ at%) alloys. It was also recognized that super-cooled liquid region was further extended. The maximum value is 50.2 K at 4 at% Al. Bulk glassy rods of 1 mm diameter can be successfully cast for this composition. These alloys also exhibit superior soft magnetic properties. As the Al content increases, the saturation magnetization ($I_s$) slightly decreases from 1.22 to 1.18 T; the coercive force ($H_c$) decreases from 3.3 to 2.2 A/m and the maximum permeability ($\mu_m$) greatly increases from 137,000 ($x = 3$) to 208,000 ($x = 5$) [18].

Carbon was then further added to replace P in the compositions: Fe$_{74}$Al$_4$Sn$_2$P$_{12-x}$Si$_4$B$_4$C$_x$ ($z = 1-4, 6$). Rod samples were also prepared. Fig. 1 shows the X-ray diffraction patterns taken from the transverse cross sections of these alloys. We can see that alloys with compositions Fe$_{74}$Al$_4$Sn$_2$P$_{12-x}$Si$_4$B$_4$C$_z$ ($z = 2, 6$) show bulk amorphizability with a diameter of 1 mm. We also further examined the possibility of glassy rods with larger diameters for these two compositions. As shown in Figs. 2 and 3, the Fe$_{74}$Al$_4$Sn$_2$P$_6$Si$_4$B$_4$C$_6$ alloy shows an amorphizability to form a glassy rod with diameter of 1 mm while that of Fe$_{74}$Al$_4$Sn$_2$P$_{10}$Si$_4$B$_4$C$_2$ alloy with a diameter up to 2 mm. It shows that a suitable addition of carbon atom to replace P has a great improvement in GFA. An SEM photo taken from the cut cross-section of a rod sample shows smooth surface and bright lustre without any contrast arising from crystalline phase, as shown in Fig. 4. The further increase in cast diameter to 2.5 mm causes a complete crystallization; the crystalline phases have been clarified as $\alpha$-Fe, FeP, FeB, Fe$_3$P and FeC by X-ray diffraction.

Fig. 5 shows DSC curves of Fe$_{74}$Al$_4$Sn$_2$P$_{12-x}$Si$_4$B$_4$C$_x$ ($x = 0-4, 6$) amorphous ribbons. In each curve there is a glass transition followed by a super-cooled liquid region and then an exothermic reaction, indicating the crystallization of the amorphous phase. One can see that there is a large change in $T_g$ and $T_x$ after replacing P by C. The exothermic reaction separates into two stages leading to a result that the $T_x$ greatly decreases from 788 K to about 755 K while $T_g$ decreases slightly from 742 to 735 K causing a large reduction in super-cooled liquid region ($\Delta T_x$) from about 50 K to merely about 20 K. This behaviour is quite uncommon for most Fe-based bulk amorphous alloys, which generally exhibit large super-cooled liquid region above 40 K even to 60 K; and moreover the crystallization mode is not the common single-stage mode. One can remember that there is another important criterion for achieving high glass-forming ability, i.e., highly reduced
glass transition temperature, \(T_{g_0} = T_g / T_m\). DTA was used to examine the melting point \((T_m)\) for these three alloys. The DTA curves in Fig. 6 show that the melting temperature of the \(\text{Fe}_{74}\text{Al}_{4}\text{Sn}_{2}\text{P}_{12-z}\text{Si}_{4}\text{B}_{4}\text{C}_{z} \quad (z = 0, 2, 6)\) amorphous alloys gradually decreases from 1244 to 1215 K. Comparing with the glass transition temperature \((T_g)\) as shown in Table 1, the reduced glass transition temperature \((T_{rg})\) of the \(\text{Fe}_{74}\text{Al}_{4}\text{Sn}_{2}\text{P}_{12-z}\text{Si}_{4}\text{B}_{4}\text{C}_{z}\) amorphous ribbons reaches the maximum value 0.6, which is a high value among Fe-based bulk amorphous alloys. It is thus concluded that \(T_{rg}\) is a better criterion for judging GFA of the \(\text{Fe}_{74}\text{Al}_{4}\text{Sn}_{2}\text{P}_{12-z}\text{Si}_{4}\text{B}_{4}\text{C}_{z}\) alloys.

The amorphous samples in ring shape with thickness 1 mm have been demonstrated, as shown by X-ray diffraction patterns in Fig. 7. Samples in ring form with inner diameter 5 mm, outer diameter 8 mm; and that with inner diameter 6 mm and outer diameter 10 mm are amorphous.

Besides the improvement of glass-forming ability, it is also observed that the serious brittleness of \(\text{Fe}_{74}\text{Al}_{4}\text{Sn}_{2}\text{P}_{12-z}\text{Si}_{4}\text{B}_{4}\) alloy, that hindered manipulation of amorphous ribbons into cores, was greatly improved leading to a good casting operation after adding carbon.

Hardness value of the bulk amorphous alloys slightly increases with increasing C content from HV806 to HV847.
In view of the three empirical rules for forming glassy metals, we found that they were not strictly followed in our alloys. The addition of larger Al atoms does contribute to the atomic size difference while Sn does not, since it has the same atomic size as that of Fe. However, Sn and Al elements have either a positive (Sn) or a very small negative (Al) heat of mixing with all other elements. These indicate that not all alloys with good GFA follow exactly with the three empirical rules. On the other hand, the alloy with high GFA also does not necessarily have a wide super-cooled liquid region, $T_{x}$, as already delineated above.

The atomic size of carbon is much smaller than all other constituent elements so that it easily becomes an ‘interstitial-like’ atom in the alloys. As a result, C greatly improves the degree of random-packed structure. The interaction between Al and metalloids might play a role in GFA. It is known that aluminium has a very strong bonding to metalloids forming Al-metalloid compounds such as AlP, AlB$_{12}$ and Al$_{4}$C$_{3}$ with very high melting temperature, about 2800, 2400 and 2600 K, respectively, which are much higher than those of crystalline phases. This bonding nature of Al tends to cause preferred Al-metalloid pairs within amorphous structure as a result of retarding crystallization. The addition of carbon enhances this effect.

### 3.2. Magnetic properties

Fig. 8 shows the variation of Curie temperature ($T_{c}$) with C content. As C content increases, $T_{c}$ increases from 547 to 595 K. This indicates that C slightly increases Fe–Fe distance thus an enhanced exchange interaction.

Fig. 9 shows the coercivity ($H_{c}$) of as-quenched bulk glassy rod and amorphous ribbon samples. The $H_{c}$ is quite high about 6400 A/m (80 Oe) for bulk glassy sample and is much lower about 40 A/m (0.5 Oe) in ribbon form. The saturation magnetization ($I_{s}$) increases with C replacement from 1.28 to 1.38 T for bulk glassy rod and from 1.32 to 1.42 for amorphous ribbon sample. The slight

### Table 1

Glass transition temperature ($T_{g}$), melting temperature ($T_{m}$) and reduced glass transition temperature ($T_{rg}$) of Fe$_{74}$Al$_{4}$Sn$_{2}$P$_{12-z}$Si$_{4}$B$_{4}$C$_{z}$ ($z = 0, 2, 6$) alloys

<table>
<thead>
<tr>
<th>Fe$<em>{74}$Al$</em>{4}$Sn$<em>{2}$P$</em>{12-z}$Si$<em>{4}$B$</em>{4}$C$_{z}$</th>
<th>$T_{g}$ (K)</th>
<th>$T_{m}$ (K)</th>
<th>$\Delta T_{x}$ (K)</th>
<th>$T_{rg}$ ($=T_{g}/T_{m}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z = 0$</td>
<td>736</td>
<td>1244</td>
<td>50</td>
<td>0.59</td>
</tr>
<tr>
<td>$z = 2$</td>
<td>739</td>
<td>1224</td>
<td>20</td>
<td>0.60</td>
</tr>
<tr>
<td>$z = 6$</td>
<td>710</td>
<td>1215</td>
<td>40</td>
<td>0.58</td>
</tr>
</tbody>
</table>

![X-ray diffraction patterns](image)  
Fig. 7. X-ray diffraction patterns of bulk samples in ring shape with a thickness 1 mm from Fe$_{74}$Al$_{4}$Sn$_{2}$P$_{10}$Si$_{4}$B$_{4}$C$_{2}$ alloy.

![Graph](image)  
Fig. 8. Variation of Curie temperature ($T_{c}$) with different $z$ for melt-spun Fe$_{74}$Al$_{4}$Sn$_{2}$P$_{12-z}$Si$_{4}$B$_{4}$C$_{z}$ ($z = 2, 4, 6$) amorphous ribbons.
decrease in $I_h$ for bulk glassy sample arises from the difficulty in bringing to saturation during measurement.

The resistivity ($\rho$), which is the higher the better in transformer applications, increases linearly from 175 to 188 $\mu\Omega$-cm with increasing Al content in Fe$_{76-x}$Al$_x$Sn$_2$P$_{12}$Si$_4$B$_4$ alloy, while decreases to 168 $\mu\Omega$-cm with increasing $z$ of the Fe$_{74}$Al$_{12-z}$Si$_4$B$_4$C$_2$ amorphous ribbons.

The amorphous ring thereof with a micro-breakage shows a single-turn electrical inductance 168 nH/g, which was increased to 277 nH/g after stress-relief annealing. Among the studied alloys, Fe$_{74}$Al$_{12}$Sn$_2$P$_{10}$Si$_4$B$_4$C$_2$ and Fe$_{74}$Al$_4$Sn$_2$P$_6$Si$_4$B$_4$C$_6$ alloys show high glass-forming ability, good castability and excellent magnetic properties thus are potential for high-frequency applications in which the wound cores made of ribbons can be replaced by as-cast amorphous cores to ease the production.

4. Conclusions

Glass-forming ability was much improved by suitable modifications of the Fe$_{80}$P$_{12}$Si$_4$B$_4$ base alloy with Al, Sn and C. The maximum attainable diameter of bulk glassy rods is 2 mm for the Fe$_{74}$Al$_{12}$Sn$_2$P$_{10}$Si$_4$B$_4$C$_2$ alloy and 1 mm for the Fe$_{74}$Al$_{12}$Sn$_2$P$_6$Si$_4$B$_4$C$_6$ alloy. Alloys show a narrower super-cooled liquid region of about only 20 K, while, however, has a highly reduced glass transition temperature about 0.6. With increasing carbon content, the magnetic properties of Fe$_{74}$Al$_{12}$Sn$_2$P$_{12-z}$Si$_4$B$_4$C$_2$ amorphous rods are: saturation magnetization 1.28–1.38 T, coercive force about 40 A/m, Curie temperature 547–595 K. The electrical resistivity slightly decreases from 181 to 168 $\mu\Omega$-cm with increasing $z$ value. Hardness slightly increases with C addition from HV806 to HV847. The amorphous ring thereof with a micro-breakage shows a single-turn electrical inductance 168 nH/g, which was increased to 277 nH/g after stress-relief annealing. Among the studied alloys, Fe$_{74}$Al$_{12}$Sn$_2$P$_{10}$Si$_4$B$_4$C$_2$ and Fe$_{74}$Al$_4$Sn$_2$P$_6$Si$_4$B$_4$C$_6$ alloys show high glass-forming ability, good castability and excellent magnetic properties thus are potential for high-frequency applications in which the wound cores made of ribbons can be replaced by as-cast amorphous cores to ease the production.

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