Composition design of high Bs Fe–based amorphous alloys with good amorphous-forming ability

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Abstract

The composition design rules for high $B_s$ amorphous alloys are introduced from the binary phase diagram, atomic size and the effects of amorphous forming elements on magnetic performance and ribbon manufacturability. The effects of metalloid elements on amorphous-forming ability and magnetic properties as well as origin of the excellent properties for high Fe content Fe$_{83}$(Si,B,P,C)$_{17}$ amorphous alloys are explored. Based on the similar Fe content of Fe–B, Fe–P and Fe–C eutectic alloys, the alloy systems with the combination of Fe, B, P, C and Si are beneficial to the achievement of high $B_s$ and amorphous-forming ability. With the addition of Si, P and C in Fe$_{83}$B$_{17}$, the amorphous-forming ability and the soft-magnetic properties improve clearly. The critical wheel speed decrease from 54 m/s to 12 m/s and the maximum thickness increase to 76 mm. The improvement of the amorphous-forming ability is discussed in term of the competition effect and the eutectic theory.

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1. Introduction

Soft-magnetic materials play important functional role in electronic and magnetic products which greatly affect the human production and living ways. In the 21st century, stronger, lighter, higher energy efficient and more silent are the long-term targets and key challenges of device development [1]. This requires constant enhancement of magnetic performance containing higher effective permeability ($\mu_e$) and saturation flux density ($B_s$), lower coercivity ($H_c$) and core loss. After a centennial development, many kinds of soft magnetic materials have been developed and some have been widely used in different fields according to their unique performance [2]. Fig. 1 shows relationship between $\mu_e$ at 1 kHz and $B_s$ for the representative soft magnetic materials. Among these materials, silicon steels and ferrites still dominate the markets. Although lower in $B_s$ and effective permeability than metallic materials, their far higher resistivity continue to make ferrites advantageous for medium–high frequency applications which are unlikely to be supplanted, particularly above 1 MHz [3]. However, for the widest used silicon steels, the dominate positions in electricity generation, transmission and transformation are being challenged by the Fe-based amorphous and nanocrystalline alloys which exhibit much higher permeability as well as lower core loss [4]. It has been proved that the low load loss of transformer with amorphous alloy core is only about 1/4 of that with silicon steel cores [5]. The motors with amorphous alloy core can have high speed and energy density much easier [6]. Together with the low energy consumption and high productivity, amorphous alloys and its nanocrystalline derivations are generally acknowledged as double green products for production and application. Moreover, for the deficiencies like bigger size and higher noise of the currently commercial amorphous alloy cores, we can also overcome by developing new alloys with higher properties or by adjusting core design [7]. With the maturity of wide ribbon production, core design, heat treatment, machining technologies, the production and application of amorphous alloys will undoubtedly have rapid growth in the near future.

Great efforts have been devoted to develop new amorphous alloys and optimize the properties by tuning composition,
production process, heat treatment modes for stress relieving and nanocrystallization since 1967. Many ferromagnetic amorphous alloy systems like FePC [8], FeSiB [9], FePb, FeSiBc [10] as well as Co-based and FeNi-based counterparts [11] were developed for ribbon production and application [12]. As research hotspots in the past two decades, a lot of bulk metallic glasses (BMGs) with high amorphous-forming ability (AFA) and nanocrystalline alloys with good magnetic performance were developed which expanded the application fields and the properties range [13]. However, the obtaining of high AFA for BMGs is always at the expense of the Bs and cost [14]. On the other hand, high Bs amorphous alloys like Fe96B4C2 and the amorphous precursor of Fe80~85Si(B,P,C)Cu nanocrystalline alloys are hard to be made into wide ribbons by using the current production machine and process, because of the low AFA. Therefore, development of alloys with high Bs and adequate AFA is tremendously desired. Exploring the effects of amorphous forming elements on magnetic properties and AFA of high Bs alloys as well as building composition design rule have great meaning. In addition, since the glass transition and supercooled liquid region for most high Fe content compositions have vanished, the commonly used AFA criterions in BMGs development like ΔTf, Tg and γ correlated to the Tfe are no longer useful [15]. Further investigation is necessary to obtain a reliable and useful criterion to reflect the AFA.

In our recent work, high Fe content Fe35Cx(B,P,C)50 amorphous alloys with excellent magnetic properties and high AFA were successfully developed by introducing new amorphous-forming elements and adjusting composition [16]. Here, the composition design rule for high Bs amorphous alloys is introduced from the binary phase diagram, atomic size and the effects of amorphous forming elements on magnetic performance. The effects of metalloid elements on AFA and magnetic properties as well as origin of the excellent properties are explored.

2. Composition design

Since the amorphous alloys discussed here are developed for wide ribbon production and application, the critical cooling rate and needed AFA are set by the parameters of production machine and planar flow melt spinning process. A new major element selecting rule is used here from the comprehensive consideration of magnetic properties, the cost, the base of AFA need and the mass ribbon manufacturability, different from the former empirical rules for searching compositions likely to yield BMGs [18]. According to the previous reports, most elements on the periodic table shown in Fig. 2 are easily excluded from high Bs Fe-based soft magnetic alloys and the excluding rules are elaborated below.

1. Gas elements.
2. Positive or small negative mixing enthalpies with Fe [19].
3. Precious metal elements.
4. Element which is prone to form refractory compounds with Fe. Refractory compounds such as oxide inclusions will act as hetero nuclei which will decrease the AFA greatly.
5. Rare earth elements which have been reported will drastically decrease the Bs and toughness [20,21].
7. Less common element.
8. Toxic element.
9. Anti-ferromagnetic element which can improve the anti-corrosion properties will drastically decrease the Bs.

The major element candidates of almost all amorphous alloys with high AFA and magnetic properties are shown in Fig. 3. These elements have big negative mixing enthalpies with Fe. According to the relationship between atomic numbers and atomic radius, the alloy systems like FeSiB [9], FePC [8], FeSiBp [14], FeSiB(Nb,Mo,Zr,Ta) [22], FeMoPc/Si [23], FeNBY [20] and FeAlPC(Si,Ga) [9] meet the atomic size and mixing enthalpy rules for the AFA. It has been pointed out that large (L) and small atoms (S) may form highly packed atomic configuration and reinforced “backbone” structure in the amorphous structure, resulting in the enhancement of the stability of the undercooled liquid, and further suppression of crystallization [24]. On the other hand, the addition of metallic elements with large atomic number will greatly decrease the Bs by reducing the unfilled 3d orbit of Fe atoms and deteriorating the ferromagnetic exchange interaction by enlarging the distance between magnetic atoms. The addition of Al will increase the melt viscosity and the amount of alumina slag which are really harmful for ribbon production. The most representative ferromagnetic alloy systems are aggregated in the inset of Fig. 3. There were distinctive characteristics in the alloy systems with and without metallic amorphous forming element. As a consequence, it is better for us to select the alloy system without metallic amorphous forming elements for the production of wide ribbon with high Bs.

According to upper analysis, we can have thirteen combinations with Fe, Si, B, P and C. However, the alloys like FeSi and FeC have poor AFA. Only FeB, FeSiB, FeBC [25], FePC [8], FeSiBP [14], FeSiBc and FeSiBPC [26] systems can be made into single amorphous state by melt spinning method. FeSiB and FeSiBc amorphous alloys with high Bs have been widely used with the trademarks of Metglass 2605SA1 and Metglass 2605SHB1 [7]. It has been proved that the optimal Fe content are about 80 and 82 at.% [7] for FeSiB and FeSiBc amorphous alloys, based on the AFA need of planar flow melt spinning process [27]. The FeSiBp and FeSiBc alloys with Fe content about 76 at.% has been proved have high AFA and could be made into bulk samples in recent years [14,26,28]. In order to develop high Bs amorphous alloys by increasing the Fe content, the FeSiBP and FeSiBPC alloy systems with high AFA are two promising candidates.

The Fe content was selected according to the phase diagrams of Fe–B, Fe–P, Fe–C and Fe–Si shown in Fig. 4. It is clear that the eutectic point of Fe–B, Fe–P, Fe–C are 17%, 17% and 17.1%, respectively. The eutectic point of Fe–Si is higher than 30%. In the full
range of Fe-based amorphous alloys, the Fe and Si are mutually soluble. In addition, the liquidus temperature of eutectic alloys with P and C are lower than that of Fe83B17. Therefore, we can speculate that the alloys with 17% amorphous forming elements will exhibit high AFA and Bs. Since the high content addition of P and C will drastically decrease the Bs and change the ribbon production parameters, minor substitution is commonly used for composition revision [29]. In this paper, Fe83B17, Fe83B15Si2, Fe83B14Si2C1, Fe83B13Si2P3 and Fe83B11Si2P3C1 were prepared. The effects of B, Si, P and C on the AFA as well as the magnetic properties are discussed.

3. Experiment procedures

Multicomponent alloy ingots with nominal compositions of Fe83B17, Fe83B15Si2, Fe83B14Si2C1, Fe83B13Si2P3, Fe83B11Si2P3C1 were premelted by induction melting the mixtures of pure Fe (99.99 mass%), crystalline B (99.5 mass%), pre-alloyed FeP and FeC ingots under a high-purity argon atmosphere. Ribbons with width of about 1 mm and thickness of about 20–100 μm were prepared by single copper roller melt-spinning method. The thickness was controlled by changing the wheel speed. The amorphous structure was identified by X-ray diffraction (XRD) with Cu Kα radiation. Thermal physical parameters including Curie temperature (Tc) and crystallization temperature (Tx) of the amorphous alloys were examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The liquidus temperature (Tl) was measured with a DSC by cooling the molten alloy samples at a low cooling rate of 0.067 K/s to reduce the influence of undercooling. As the magnetic properties depend on the sample sizes, in the interest of clarification the intrinsic soft-magnetic properties of this amorphous alloy system, ribbon samples with similar size mentioned above were used for measurement. Saturation flux density (Bs) under a maximum applied field of 800 kA/m was measured with a vibrating sample magnetometer (VSM). Coercivity (Hc) was measured with a DC B–H loop tracer under a field of 800 A/m. Effective permeability (μe) at 1 kHz was measured with an impedance analyzer under a field of 1 A/m. All of the ribbon samples for magnetic property measurements were annealed for 1 h in order to reduce the influence of inner stress on soft-magnetic properties through structural relaxation. The density was measured by the Archimedean method. All the measurements were performed at room temperature.

Fig. 2. Selectively excluded elements for high Bs soft-magnetic amorphous alloys.

Fig. 3. Relationship between atomic numbers and atomic radius of commonly used elements in amorphous soft-magnetic alloys.

Fig. 4. Binary phase diagrams of Fe–B, Fe–P, Fe–C and Fe–Si.
4. Result and discussion

Fig. 5 shows DSC curves obtained from the Fe\textsubscript{83}B\textsubscript{17-a-b-c}Si\textsubscript{P}C\textsubscript{c} master alloys. The heating rate of the melting process and the cooling rate of the solidification process are commonly used 0.67 K/s and 0.067 K/s, respectively. The onset and off-set temperatures of the melting endothermic event shown in the heating section were designated by \(T_m\) and \(T_{lm}\). The onset temperature of the solidification exothermic event shown in the cooling section is designated by \(T_s\). With the addition of Si\textsubscript{2}, Si\textsubscript{2}C\textsubscript{1}, Si\textsubscript{2}P\textsubscript{3} and Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1}, \(T_m\) and \(T_{lm}\) decrease gradually. The fusion enthalpies obtained from the area of the fusion peak in DSC data decrease clearly, which indicates the lower binding energy of the crystalline phases. As can be seen from the solidification curves, the crystallization peak splits with the increase of Si implies the diversity of precipitation phases. In addition, it is clear that the changes of \(T_m\), \(T_{lm}\) and \(T_s\) show different trends. As the solidification process is quasi-static because of the low cooling rate, \(T_s\) reflect the liquidus temperature and undercooling. The undercooling determined by the \(T_{lm}-T_{ls}\) of the Si\textsubscript{2}, Si\textsubscript{2}C\textsubscript{1}, Si\textsubscript{2}P\textsubscript{3} and Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1} doped alloys decreases which can be related to the structure differences between the liquid and primary solid phases.

Single roller melt-spinning method was used to evaluate the AFA of these alloys. Ribbon thickness was controlled by changing the wheel speed. The critical thickness and wheel speed were selected as the indexes of AFA. In order to decrease the errors, all experiments with critical wheel speed were performed at least three times. Fig. 6 shows the XRD patterns taken from the free surface of melt-spun Fe\textsubscript{83}B\textsubscript{17}, Fe\textsubscript{83}B\textsubscript{15}Si\textsubscript{2}, Fe\textsubscript{83}B\textsubscript{14}Si\textsubscript{2}C\textsubscript{1}, Fe\textsubscript{83}B\textsubscript{12}Si\textsubscript{2}P\textsubscript{3} and Fe\textsubscript{83}B\textsubscript{11}Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1} alloy ribbons with critical thickness. The XRD patterns exhibit only diffuse halos, and no sharp diffraction peaks corresponding to crystalline phases are visible. It is clear that the AFA increase clearly with the addition of Si, C and P. Fe\textsubscript{83}B\textsubscript{12}Si\textsubscript{2}P\textsubscript{3} and Fe\textsubscript{83}B\textsubscript{11}Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1} alloy exhibit high AFA and can be made into single amorphous phase by using the common speed (18–25 m/s) of wide ribbon production. This result confirms the effectiveness of composition design rules for Fe-based amorphous alloys we described in part 2.

In order to investigate the effect of B, Si, C and P on the properties of high Fe content amorphous alloys, we choose the alloy ribbons made with wheel speed higher than critical values except the Fe\textsubscript{83}B\textsubscript{17}, Fe\textsubscript{83}B\textsubscript{15}Si\textsubscript{2}, Fe\textsubscript{83}B\textsubscript{14}Si\textsubscript{2}C\textsubscript{1}, Fe\textsubscript{83}B\textsubscript{12}Si\textsubscript{2}P\textsubscript{3} and Fe\textsubscript{83}B\textsubscript{11}Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1} alloy ribbons made with 35 m/s were used. All of the melt-spun ribbons used for thermal and magnetic tests confirmed in the X-ray diffraction patterns are composed of a full amorphous phase without crystallization. Fig. 7 shows the DSC curves exhibiting the crystallization behavior of the Fe\textsubscript{83}B\textsubscript{17-a-b-c}Si\textsubscript{P}C\textsubscript{c} amorphous alloys. No obvious glass transition can be detected for all alloys. As enlarged in the inset, \(T_c\) increase with the addition of Si and C, and decrease with the addition of P. All alloys exhibit lower \(T_c\) compared with that of the commercial FeSiB and FeSiBC alloys [16]. In addition, the Fe\textsubscript{83}B\textsubscript{17} amorphous alloy exhibits only one sharp crystallization exothermic peak. The Si added amorphous alloys have two exothermic peaks. As shown in the enlarged DSC figure, the exothermic peaks of the Fe\textsubscript{83}B\textsubscript{12}Si\textsubscript{2}P\textsubscript{3} and Fe\textsubscript{83}B\textsubscript{11}Si\textsubscript{2}P\textsubscript{3}C\textsubscript{1} amorphous alloys are wider than that of the other one. Accordingly, we can speculate that the precipitation phases of the Si added alloys are more complicated.
Fe₈₃B₁₁Si₂P₃C₁ and Fe₈₃B₁₁Si₂P₃C₁ amorphous alloys are slower. Since the Tₓ₁ do not changes clearly, all alloys with high Fe content exhibit the advantages of low Tₓ and large Tₓ₁-Tₓ which indicates a lower annealing temperature and large annealing temperature range [16].

Magnetic properties of the Fe₈₃B₁₁-Si-P-C amorphous alloys subjected to stress relief annealing are investigated systematically. Table 1 summarizes the thermal stability and magnetic thermal parameters, magnetic properties, critical wheel speed and thickness of the Fe₈₃B₁₁-Si-P-C amorphous alloys. Only slight changes of Bc can be detected. All alloys exhibit a high Bc. It is noted that the soft magnetic properties changes greatly. The Hc of Fe₈₃B₁₁Si₂, Fe₈₃B₁₁Si₂P₃, and Fe₈₃B₁₁Si₂P₃C₁ alloys are much lower than that of the Fe₈₃B₁₇. The low Hc and high effective permeability (µₑ) at 1 kHz of alloys with high AFA confirms the high amorphicity and stability of phase. Hence, we can also draw a conclusion that excellent soft magnetic properties can be gained, so long as we meet the needed AFA when developing new Fe-based amorphous alloys.

It is now well established that amorphous formation in metallic liquids is essentially a competing process between liquid phases and the crystalline phases [30]. Any factors which can increase liquid phase stability or suppress crystallization would enhance the AFA. In order to investigate the effect of Si, P and C addition on the crystallization process and thermal stability of the amorphous phase, XRD measurements were carried out for the alloy ribbons with as-quenched and annealed state. Fig. 8 shows the XRD patterns of the as-quenched samples prepared with wheel speed lower than the critical values. The precipitated phases of the Fe₈₃B₁₇ alloy are Fe₂B and Fe₃B. For the alloys with Si addition, the Fe₃B is suppressed and α-Fe(Si) shares the maximum proportion. In addition, the Fe₃B transforms to Fe₃(B,P) for the P containing alloys, implying that the lattice parameters enlarges and some B atoms are substituted by P atoms. Since Fe₃(B,P) contains three different elements and its structure is more complex, the crystallization process requires longer range atom rearrangements of constituent elements. As proved, the precipitation of α-Fe(Si) phase always undergoes competing process [31]. All of these will increase the thermal stability of molten alloy and the AFA.

Fig. 9 shows the XRD patterns of the Fe₈₃B₁₅, Fe₈₃B₁₃Si₂ and the Fe₈₃B₁₁Si₂P₃C₁ alloy ribbons annealed at 440 °C for 10 min. For the Fe₈₃B₁₇ alloys without Si, the only eutectic peak is identified as hard-Fe₃Si crystals and depress the formation of Fe₂B and Fe₃(B, P) which have been verified as hard-magnetic phases. The formation of fine α-Fe(Si) phases or clusters without other phases is good for the soft-magnetic properties [32]. Together with the high AFA, it is easy to understand the excellent magnetic performance of the Si containing alloys.

First, we discuss the effects of metalloid elements on magnetic properties. The improvement of soft-magnetic properties including Hc and µₑ can be explained from the aspects of increasing AFA and transformation of primary phase to α-Fe(Si). Bitoh et al. has found the alloy system with high AFA will result in high degree of amorphicity and structural homogeneity which may act as quasi-dislocation dipoles (QDDs) and domain-wall pinning sites [33]. As shown in Fig. 7, Tc increases with the addition of Si and C, and decreases with the addition of P. This fact implies that the Tc of Fe-based amorphous alloys cannot be explained only by the simple charge transfer model and it is necessary to consider other factors such as the size of metalloid atoms and the short-range order

<table>
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<th>Constitution</th>
<th>Thermal properties</th>
<th>Magnetic properties</th>
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<tr>
<td></td>
<td>Tc (°C)</td>
<td>Tₓ₁ (°C)</td>
</tr>
<tr>
<td>1 Fe₈₃B₁₇</td>
<td>325</td>
<td>459</td>
</tr>
<tr>
<td>2 Fe₈₃B₁₁Si₂</td>
<td>327</td>
<td>453</td>
</tr>
<tr>
<td>3 Fe₈₃B₁₃Si₂C₁</td>
<td>328</td>
<td>447</td>
</tr>
<tr>
<td>4 Fe₈₃B₁₁Si₂P₃</td>
<td>322</td>
<td>457</td>
</tr>
<tr>
<td>5 Fe₈₃B₁₁Si₂P₃C₁</td>
<td>323</td>
<td>454</td>
</tr>
</tbody>
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Table 1: Thermal parameters, magnetic properties, critical wheel speed and thickness of the Fe₈₃B₁₁-Si-P-C amorphous alloys.
variations. In Fe-based alloys, B and P atom are prone to form compounds or short-range order with Fe. Si and C atom are interstitial atoms. The substitution of B by P will enlarge the distance of the Fe atoms which can also be proved by the change of density. The substitution of B by Si and C will decrease the distance of the Fe atoms which will lead to increase of exchange coupling interaction. The magnetic moment changes with adding of P, Si, B and C can be interpreted from the number of electron transfer from metalloid atom to 3d shell of Fe atom. For B, C, Si and P, the outermost electrons are 2p^1, 2p^2, 3p^2 and 3p^3, respectively. The B, C, Si and P of the alloys in this work does not change clearly due to the minor addition.

Then we explore the mechanism of the increase of AFA. The reasons are as follows: (1) According to the composition design rules from the binary phase diagram, atomic size and the effects of amorphous forming enhance of the stability of the undercooled liquid, and further suppresses crystallization. (2) Fe₈₃B₁₇, Fe₈₃B₁₅Si₂, Fe₈₃B₁₄Si₂C₁, Fe₈₃B₁₂Si₂P₂, Si₈₃B₁₂Si₂P₂C₁ alloys were designed according to the two binary phase diagrams in Fig. 4. A deep eutectic point is achieved by combining the Fe-B, Fe-P and Fe-C alloys with similar Fe content, which can be seen from the decreasing Tₘₑₙ, Tₘₑ₀ in Fig. 5 [34]. From the thermodynamic viewpoint, the driving force for crystal nucleation and growth below the eutectic temperature is comparatively small. (3) With the substitution of Si, the primary phase transforms from Fe₃B to α-Fe(Si) which can increase the competing effect. In addition, the addition of P and C make the boride precipitation phase more complexity.

5. Conclusion

According to the composition design rules from the binary phase diagram, atomic size and the effects of amorphous forming elements on magnetic performance, high Bₙₗ amorphous alloy systems containing FeB, FeSiB, FeSiBP, FeSiBC and FeSiBPC are designed. The Fe content is determined as 83 at% in the light of the similar Fe content of Fe₃B, Fe₃P and Fe₃C eutectic alloys. The alloy systems with the combination of Fe, B, P, C and Si is beneficial to the achievement of high Bₙₗ and AFA. The effects of metallicloid elements on AFA and magnetic properties as well as origin of the excellent properties are explored. With the addition of Si, P and C in Fe₈₃B₁₇, the critical wheel speed decrease from 54 m/s to 12 m/s and the maximum thickness increase to 76 μm. The improvement of the AFA is owing to the competition effect of the α-Fe(Si) precipitation and the approach of deep eutectic point. The excellent soft-magnetic properties are attributed to the high degree of amorphyic and structural homogeneity.

Acknowledgments

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