Development of FeNiNbSiBP bulk metallic glassy alloys with excellent magnetic properties and high glass forming ability evaluated by different criterions

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\textbf{A B S T R A C T}

Fe\textsubscript{38}Ni\textsubscript{38}Nb\textsubscript{2.5}B\textsubscript{21.5}P\textsubscript{x}Si\textsubscript{y} (x, y = 1–8) bulk metallic glassy alloys with high glass forming ability and excellent magnetic properties were developed. Bulk samples with maximum diameters of 3 mm are fabricated by copper mold casting method. The glassy alloys have large $\Delta T_g$ of 40–70 K. The alloys exhibit excellent magnetic properties like extremely low $H_c$ of 0.5–0.8 A/m, high $\mu_e$ of 1.6–2.85 $\times 10^4$ and comparatively high $B_s$ of 0.6–0.8 T which changes regularly with the content variations of P, B and Si. By ascertaining applicability of the empirical GFA criterions, $T_{rg}$, $\alpha$, $\beta$ and $\gamma$ can be used in evaluating the GFA of FeNiBSiPNb system alloys.

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1. Introduction

Since the Fe–C–P alloy was firstly found in 1967 \cite{1}, ferromagnetic metallic glassy alloys have attracted increasing interests because of their excellent magnetic performances including high saturation magnetic flux density ($B_s$), low coercivity ($H_c$), high permeability and low core loss \cite{2}. By devoting subsequent great efforts, a variety of ferromagnetic metallic glassy alloys have been explored and some have been widely used. According to their unique performance, the representative Fe-based, Co-based and FeNi-based metallic glassy alloys ribbons under the trademarks of METGLAS and VITROVAC \cite{3} are used in different and wide fields. The FeNi-based amorphous alloys with better mid-high frequency characteristic than Fe-based alloys are mainly used to substitute permalloys in sensors, magnetic shielding, switching transformers, anti-theft label etc. Especially after the first Fe-based bulk metallic glassy alloy (BMG) was casted in 1995 \cite{4}, other outstanding advantages containing high strength, high corrosion resistance, and sewage degrading et al. remarkably expand the potential application fields and make ferromagnetic element based metallic glasses hotspots.

Nevertheless, there seems to be contradictions among saturation flux density ($B_s$) and glassy forming ability (GFA), fracture strength and plastic deformation capacity \cite{5,6}. Moreover, although a few empirical criterions based on the characteristic temperatures have been proposed and verified for certain particular systems, the development for new ferromagnetic BMG formers is mainly based on try and error experiments which are time consuming and costly \cite{7}. The mechanism and effect of composition on these key properties have been subjects of numerous studies to further improve the performance. According to the reports of Yang and Liu et al. \cite{8,9}, the glass transition and mechanical yielding have the same thermodynamic origin. The glassy alloys with low glass transition temperature ($T_g$) are more likely to have large plastic strain. It has
been proved that the increase of the content of ferromagnetic element is the most important approach for increasing the Bs which always lead to the decrease of Tm and the GFA [10]. It is hence possible to gain good magnetic and mechanical properties in high FeNi content glassy alloys which have the lowest Tm [5]. Therefore, enhancement of GFA and preparation of high FeNi content BGAs would be tremendous desired. The alloys which can be made into bulk sample not only ensure the fabrication stability of ribbon during glass formation, subsequent heat treatment processes and shaping operations, but also make ferromagnetic BGAs promising structure materials.

In our previous work, FeNiBPNb system glassy alloys with high GFA and magnetic properties were developed by using similar atom substitution method [11,12]. In this paper, Si is introduced in order to enhance the GFA and enlarge composition range. The effects of metalloid elements on the GFA, GFA criterion indexes and magnetic properties are investigated systematically. FeNiNbSiB P bulk metallic glassy alloys with high glass forming ability and excellent magnetic properties were exploited. To ascertain the applicability of the GFA criterions for ferromagnetic glassy alloys, the compositional dependence of the GFA criterions for ferromagnetic glassy alloys, the compositional ranges correlated to critical size of samples and commonly used GFA criterions are carefully compared, where both of these investigations complement each other in obtaining the in-depth insight into the soft magnetic metallic glass.

2. Experiment procedures

36 alloy ingots with nominal compositions of Fe39Ni39Mo4Si6B12 (1) and Fe39Ni39Mo4Si6B12 (3). All of the glassy alloys exhibit glass transition, followed by a supercooled liquid region and then crystallization. It is obvious that the supercooled liquid region (\(\Delta T_g\)) at the glass transition region of the Fe38Ni39Nb2.5B15.5Si3 alloys is much higher than that of the representative Fe39Ni39Mo4Si6B12 alloy [11]. The introduction of Si is effective in enhancing the thermal stability of the supercooled liquid. In addition, Fe38Ni39Nb2.5B15.5Si3, Fe39Ni39Mo4Si6B12, and Fe39Ni39Mo4Si6B12 glassy alloys exhibit two, one and three distinct crystallization exothermic peaks, respectively.

Compositional dependence of Tg obtained from the DSC curves of Fe38Ni39Mo4Si6B12 (2) and the compared alloy Fe39Ni39Mo4Si6B12 (3). metallic glassy alloys subjected to stress relief annealing at Tg=50 K for 10 min are investigated systematically. Compositional dependence of Bs are depicted in Fig. 3. Consistent with the previous reports in Fe-based, FeCo-based alloy systems, Bs changes regularly in the range of 0.6–0.8 T with the content variations of P, B and Si which has been explained by the electron transfer model [13,14]. Graham et al. have pointed out that the outermost electrons could transfer from the metalloid elements to fill the unfilled d shell of the transition metal elements which will decrease the moment per metal atom [14]. In this alloy system, B, Si and P hold 1, 2 and 3 s electrons, respectively. It is clear that low P content alloys exhibit higher Bs. In addition, the alloys exhibit excellent soft-magnetic properties like extremely low Hc of 0.5–0.8 A/m and high \(\mu_s\) of 1.6–2.85 \(\times 10^4\). Although the Hc and \(\mu_s\) values show considerable scatter which is dependent on factors other than alloy composition, we can draw a conclusion that the developed Fe39Ni39Mo4Si6B12 metallic glassy alloys exhibits good magnetic performance in a large composition range. According to the theoretical analysis on the basis of domain-wall movement of Bith et al. [15], the excellent soft magnetic properties always originate from the much higher packing density of the bulk glassy alloys than that of metallic glass.
the conventional amorphous alloys. The low $H_c$ and high $\mu_e$ imply the Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ alloys may exhibit high GFA which will realize the low density of the quasi-dislocation dipole-type elastic stress sources or the low pinning force due to the elastic stress.

The compositional dependence of GFA of the Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ alloys were investigated then. We tried to produce cylindrical glassy rods with different diameters up to 4 mm by the copper mold casting method. Fig. 4 shows critical diameters for Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ metallic glassy alloys. It is clear that the alloys in a wide composition range have high GFA and most of them can be made into bulk samples. The high GFA composition range are enlarged and the maximum GFA are enhanced by introducing Si. The alloys around Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{15.5}$P$_3$Si$_3$ exhibit the highest GFA and can be made into 3 mm diameter rods. The GFA of the alloys deviating the optimal composition range decreases regularly. Compared with the representative Fe$_{39}$Ni$_{39}$Mo$_4$Si$_6$B$_{12}$ alloy which can be made into ribbon sample only, the good combination of high glass-forming ability and good soft magnetic properties characterized especially low $H_c$ and high $\mu_e$ indicates the possibility of future mass production as new low loss material.

In order to explore the origin of high GFA of the Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ alloys, the melting and solidification behaviors were investigated. Fig. 5 presents compositional dependence of $T_l$ obtained from the DSC curves of Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ master alloys. The $T_l$ changes gradually with the variation of B, Si and P contents, and reaches a minimum value of about 960 °C for the alloys around Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$P$_4$Si$_4$. In addition, the temperature interval of exothermic peaks decrease markedly with the decrease of $T_l$ indicating that the alloys are close to the eutectic point in this alloy system. Compared with that of the basic alloy Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{15.5}$P$_6$ and the representative alloy Fe$_{38}$Ni$_{38}$Mo$_4$Si$_6$B$_{12}$, the alloys exhibit lower $T_l$ in a wide compositional range indicating that they approach a deep eutectic point.

According to the thermal parameters obtained from DSC measurement, we calculate the commonly used criterions [7,16] for predicting GFA including $\Delta T_x$ ($=T_x-T_g$), $T_x$ ($=T_l/T_g$), $\alpha$ ($=T_x/T_l$), $\beta$ ($=T_g/T_l$ and $T_g/T_l$) and $\gamma$ ($=T_x/(T_g+T_l)$) for finding a proper GFA criterion in developing new ferromagnetic BMG systems. Compositional dependence of $\Delta T_x$ obtained from the DSC curves of the Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$C$_0$xC$_0$yP$_x$Si$_y$ metallic glassy alloys.
Fig. 6. Metalloid content dependence of $\Delta T_x$ for Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$Si$_y$P$_x$ metallic glassy alloys.

Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$Si$_y$P$_x$ grassy alloys is displayed in Fig. 6. Dislike the linear change of $T_g$, the $\Delta T_x$ increases first and then decreases with the increase of Si content for the low P alloys. The $\Delta T_x$ increase slightly with the increases with the P content. It is clear that the alloys with high P content are prone to have larger $\Delta T_x$. In a wide compositional range, the alloys exhibit large $\Delta T_x$ of more than 50 K which are much larger than that of Fe$_{40}$Ni$_{40}$P$_6$B$_{18}$, Fe$_{40}$Ni$_{38}$Mo$_4$B$_{18}$ and Fe$_{39}$Ni$_{39}$Mo$_4$Si$_{12}$ [11]. Therefore, the supercooled liquid of Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$Si$_y$P$_x$ glassy alloy developed in this paper exhibits much better stability.

Fig. 7 shows metalloid content dependence of $T_{rg}$, $\alpha$, $\beta$ and $\gamma$ for Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{21.5}$Si$_y$P$_x$ metallic glassy alloys. The alloys in a large composition range exhibit high $T_{rg}$, $\alpha$, $\beta$ and $\gamma$ values which are closed to that of the FeNiBSiNb alloys with low FeNi content [5,6]. As a consequence, it is expected that this alloy system are adjusted to a deeper eutectic point. This conforms to the enhanced GFA in Fig. 4. It is clear that the $T_{rg}$, $\alpha$, $\beta$ and $\gamma$ indexes change orderly with the increase of B, P and Si content. The composition ranges correlated to the highest $T_{rg}$, $\alpha$, $\beta$ and $\gamma$ are slightly different. The alloys around Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$Si$_3$P$_4$ exhibit the highest $T_{rg}$ of up to 0.583. The alloys around Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$Si$_3$P$_4$ exhibit the highest $\alpha$ and $\gamma$ of 0.632 and 0.400, respectively. The alloys around Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$Si$_3$P$_4$ exhibit the highest $\beta$ of 0.669.

By comparing the compositional dependence of critical diameter and GFA criterions including $\Delta T_x$, $T_{rg}$, $\alpha$, $\beta$ and $\gamma$, we can found that variation tendency and optimum composition range are different for varying degrees. The absolutely different variation tendency with the GFA indicates $\Delta T_x$ a poor index for predicting the GFA of FeNi based alloys, which is not coincident with the previous reports in FeNiBSiNb et al. alloy systems [17,18]. On the other hand,
the $T_{\text{rg}}$, $\alpha$, $\beta$ and $\gamma$ can be used as indicators in evaluating the GFA in a large composition range although the optimal composition zones are not completely overlapped. The deviation of metalloid element content is less than 2 at%. Here, it should be emphasized that the GFA evaluation experiment was carried out first and the impacts of psychological suggestion originated from thermal index analyses can be excluded. In addition, the experimenter has rich experience and the variation tendency of critical diameter are quite reliable.

It is now well proposed that glass formation in metallic liquids is essentially a competing process between liquid phases and the crystalline phases [19,20]. Any factors from thermodynamic and kinetic contributions which can increase liquid phase stability or suppress crystallization would enhance the GFA. In order to explore the effect of Si addition on the crystallization process, thermal stability of the amorphous phase and GFA, XRD measurements were carried out for the ribbon samples with as-quenched and annealed state. Fig. 8 shows the XRD patterns of Fe38Ni38Nb2.5B13.5P5Si3 glassy alloy samples annealed for 30 min at 803 K and 893 K. Samples annealed at other temperature are also identified by XRD. No crystallization can be detected from the fully amorphous structure even after annealing at 763 K for 30 min, which indicates high stability of the supercooled liquid region and wide annealing temperature range for gaining good soft-magnetic properties. With the annealing temperature increase to 803 K, single (Fe,Ni)$_{23}$B$_6$ phase with fine grain size is detected. For the sample annealed at 893 K, Fe$_3$P$_{0.37}$B$_{0.63}$ phase is precipitated. Different from that of the basic FeNiBPNb alloys with only one exothermic peak on the DSC curves [11], the crystallization processes of Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$P$_5$Si$_3$ glassy alloy show two steps, which can be summarized as follows:

$$\text{AM} \rightarrow \text{AM}^* \rightarrow (\text{Fe,Ni})_{23}\text{B}_6 \rightarrow (\text{Fe,Ni})_{23}\text{B}_6 + \text{Fe}_3\text{P}_{0.37}\text{B}_{0.63}$$

As has been well investigated, the primary Fe$_{23}$C$_6$-type phase has a complex fcc structure with a large lattice parameter of 1.12 nm including 96 atoms in the network-like structure and requires long-range atomic rearrangements, which lead to the high stability of the supercooled liquid against crystallization and GFA [21]. The precipitation of (Fe,Co,Ni)$_{23}$B$_6$ has been commonly used to explain the high GFA of FeNbB, (Fe,Co,Ni)BSiNb [22] and et al. Here, we are interested in the effects of Si addition on improvement of GFA and the change of crystallization behavior. Thermodynamic studies on the glass formation in multicomponent alloys are generally centered on the Gibbs free energy difference between liquids and primary metastable and stable crystalline phases [23]. The $\Delta G$ between an undercooled liquid and its equilibrium crystals is known as the thermodynamic driving force of the phase transition, $\Delta G = \Delta H + T\Delta S$, where $\Delta H$ and $\Delta S$ are the difference in enthalpy and entropy. For the FeNiBPNb alloys, only (Fe,Ni)$_{23}$B$_6$ phase is formed in the one step crystallization process. With the addition of Si, the crystallization process of FeNiSiBPNb alloys change from single step
to double step [24]. We can hence speculate that the energy state of primary phase (Fe,Ni)$_{23}$B$_6$ for Si containing alloys are higher than that of basic FeNiBPNb alloys. The $\Delta G$ between undercooled liquid and primary (Fe,Ni)$_{23}$B$_6$ is smaller for the Si added alloys. It is widely accepted that a small $\Delta G$ at undercooling conditions thermodynamically favors glass formation [25]. The second reason for the enhanced GFA is based on the crystallization tendency of the component. It has been proved that B, P in ferromagnetic amorphous alloys are prone to form boride and phosphide. The Nb acts as glue atom which promotes the formation of complex Fe$_{23}$C$_6$-type phase and suppresses the atom movement during crystallization. Si shows mutual solubility and does not form phases with Fe in a large content. Si always appears as interstitial atoms which will decrease the diffusion rate in crystallization process.

Then, we discuss the possible reason why empirical GFA criterions containing $T_{\text{rg}}$, $\alpha$, $\beta$ and $\gamma$ deviate a little from the critical diameter of BMG alloys fabricated by copper mold casting method. First, the GFA evaluated as critical diameter is dependent on factors other than alloy composition, e.g., on the fabrication method [26]. The violent shock in copper mold casting method may motivate the crystallization. Second, the thermal parameters are tested with low heating and cooling rate by using DSC, while the real solidification process are much faster. Last, the empirical GFA criterions are proposed with different assumption. Only if we take into account all thermodynamic and kinetic factors together, we can explain glass formation more efficiently [7].

4. Summary

FeNiNbSIP bulk metallic glassy alloys with high glass forming ability and excellent magnetic properties were developed. By introducing Si, the GFA is enhanced and the composition range is enlarged greatly. The effects of metalloid elements on the GFA, GFA criterion indexes and magnetic properties are investigated systematically. The obtained results are summarized as follows:

1. Fe$_{38}$Ni$_{38}$Nb$_{2.5}$B$_{13.5}$-$_{x}$-yP$_{x}$Si$_{y}$ (x, y = 1–8) BMG alloys with maximum diameters of 3 mm are fabricated by copper mold casting method. The glassy alloys have large $\Delta T_x$ of 40–70 K which are much larger than that of commonly used FeNi-based glassy alloys. The alloys exhibit excellent soft-magnetic properties like extremely low $H_x$ of 0.5–0.8 A/m and high $\mu_r$ of 1.6–2.85 $\times$ 10$^4$. The $B_x$ is comparatively high of 0.6–0.8 T which changes regularly with the content variations of P, B and Si. The excellent soft magnetic properties are originated from the high GFA and high stability of amorphous phase.

2. The applicability of the empirical GFA criterions is ascertained for the future development of ferromagnetic glassy alloys. The $\Delta T_x$ is proved a poor index for predicting the GFA of FeNi based alloys. On the other hand, the GFA indicators based on thermal parameter including $T_{\text{rg}}$, $\alpha$, $\beta$ and $\gamma$ can be used in evaluating the GFA of FeNiSiPnP system alloys. The deviation of metalloid element content is less than 2 at%.

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