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The positive effect of non-inert casting atmospheres on the glass-forming ability of FeMoPCBSi bulk metallic glass

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A B S T R A C T

In order to utilize non-inert casting atmospheres to improve the glass forming ability (GFA) of Fe-based bulk glassy alloys, in this work, dependence of GFA, composition and soft magnetic properties on casting atmosphere species is observed for $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy alloy. Firstly, it was found that GFA can be significantly improved by some non-inert atmospheres, as when cast under N_2/air/O_2, its critical diameter can reach to 3.5 mm, which is larger than that of sample cast in inert Ar. Moreover, the component contents on the alloy surface vary greatly with the casting atmospheres while the whole bulk composition remains almost unchanged. In addition, this Fe-based glassy alloy exhibits identical soft magnetic properties regardless of the applied casting atmospheres. The mechanism for the positive effect of non-inert atmospheres on the GFA of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy alloy may be involved with the surface properties of alloy liquid such as surface tension and the modified superficial composition.

1. Introduction

Fe-based metallic glasses are candidates for magnetic functional applications since they possess considerably magnetic properties including high saturation magnetization (B_s), low coercive force (H_c), high effective permeability, good frequency stability and low loss, etc [1–3]. However, one of the biggest obstacles for its development and application is its poverty of glass forming ability (GFA). In order to enhance the GFA, great effort and many strategies have been devoted since the first Fe-based bulk metallic glass (BMG) was founded in 1995 [4]. Generally, when the Fe-based BMGs were prepared by similar method or equipment, these strategies can be divided into two categories: one is to scavenge heterogeneous nucleation sites out of the undercooled alloy liquids (such as pure raw materials, flux melting), and the other is through adjusting the alloy composition. In addition, it is found that the casting atmospheres also have a great impact on the GFA as the alloy composition can be modified by absorbing O or other elements from the atmosphere, and O or other elements may induce formation of harmful oxides which act as heterogeneous nucleation sites or trigger the nucleation of metastable phases [5–13]. A representative and well-known example is the GFA of Zr-based BMGs could be dramatically deteriorated when the casting atmosphere contains even a small amount of O [14]. For the same reason, some non-inert atmospheres are usually discarded and pure inert Ar is widely adopted during the preparation of BMGs. Compared with Zr-based, Cu-based, rare-earth-based and Ti-based BMGs, it seems Fe-based metallic glasses are likely less sensitive to oxygen-contained casting atmosphere during the casting procedure [15] since the manufacture of Fe-based ribbons can be performed in air [16]. However, with regard to the preparation of Fe-based BMGs, using pure inert Ar as the casting atmosphere is still the most common choice. Although a few researchers have managed to prepare Fe-based BMGs in air through the formation of harmless rare earth oxides, however, unfortunately, it is at the expense of GFA [17,18].

According to Tumbull' theory [19,20], the heterogeneous

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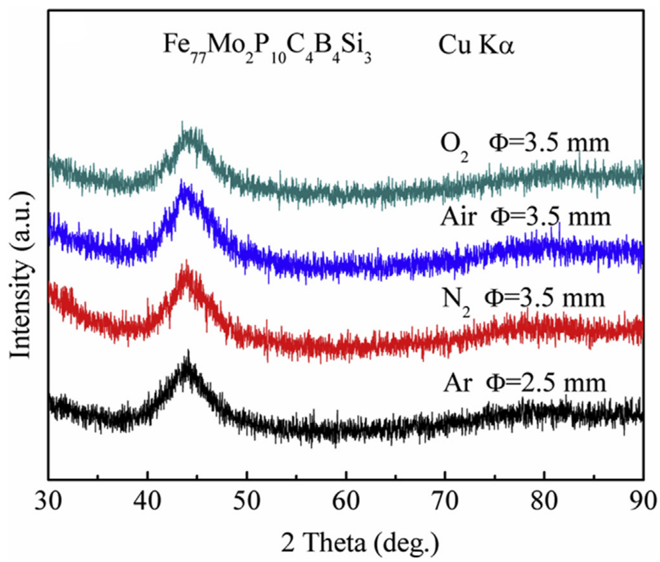

Fig. 1. XRD patterns of as-cast $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ rods prepared in Ar, N_2, air and O_2 atmospheres.

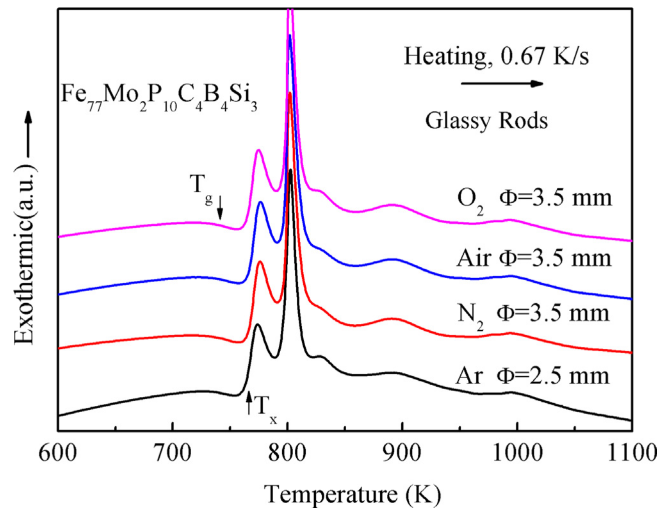

Fig. 3. DSC curves of as-cast $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy rods prepared in Ar, N_2, air and O_2 atmospheres.

nucleation rate I is related to surface tension which can be significantly influenced by the species of the atmospheres [21,22], meaning the species of the atmosphere may be involved with I or the GFA. It was also reported that O contamination (even at ppm levels) can have a dramatic effect on the surface tension of a metal alloy [23]. Inspired by this result, we decided to investigate the influence of non-inert casting atmospheres on Fe-based BMGs. An $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ alloy was reported to exhibit a critical diameter (D_{cr}) of 2.5 mm in pure Ar [24]. Subsequently, it was adopted to examine the variations of GFA, composition and soft magnetic properties with kinds of casting atmospheres in this paper. It was found that the O_2, N_2 and air benefit equivalently the GFA of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ alloy without deteriorating the soft magnetic properties. The underlying mechanism concerning the effect of non-inert casting atmospheres on the GFA was also clarified.

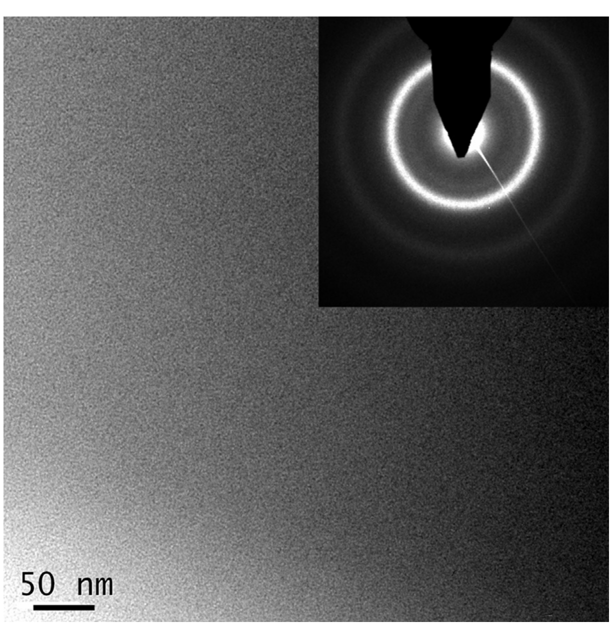

Fig. 2. TEM image and corresponding SAED pattern taken from the cross section of the as-cast $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ rod with a diameter of 3.5 mm prepared under O_2 atmosphere.

2. Experimental

A multi-component alloy ingot with a nominal composition of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ was prepared by induction melting the mixtures of pure Fe metal (99.99 wt%), pure Mo metal (99.99 wt%), pure B (99.9 wt%) and Si crystals (99.999 wt%), Fe-P alloy (99.9 wt%, 18 wt% P) and Fe-C alloy (99.9 wt%, 4.6 wt% C) under a high purified Ar atmosphere.

Cylindrical rods with a length of about 40 mm and different diameters of 2–4 mm were produced with a Rapid Quench Machine System. The casting chamber of the Rapid Quench Machine System was evacuated to ~4×10^{-3} Pa, then filled with high pure Ar, air, O_2 or N_2 to 9×10^4 Pa, respectively. Finally, the molten alloy liquid was cast into the cylindrical copper mold. In order to ensure the reproducibility, the D_{cr} was determined only after three glassy rods with the D_{cr} were obtained. Glassy ribbons with a thickness of about 20 μm were produced by melt spinning.

The as-cast rods were ground to powder at first, and then their microstructures were examined by X-ray powder diffractometer (XRD) with Cu-Kα radiation. Glass transition temperature (T_g) and crystallization temperature (T_x) were estimated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The C and P atomic concentration in the surface of alloy cast in Ar and air atmospheres were determined by Auger Electron Spectroscopy (AES, PHI 700) with a referential sputter speed of 4 nm/min of SiO_2. The contents of O and N in the master alloy and BMG samples were also measured using an EMGA-620W oxygen/nitrogen analyzer. Magnetic properties of B_s and H_c were measured at room temperature with a vibrating sample magnetometer (VSM) under an applied field of 800 kA/m and a B-H loop tracer under a field of 800 A/m, respectively.

3. Results

Fig. 1 depicts the XRD patterns of as-cast $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ rods prepared in Ar, N_2, air, and O_2 atmospheres under chamber pressure of 9×10^4 Pa. From Fig. 1, it can be found all the XRD patterns with different diameters prepared in corresponding atmosphere consist of only a typical halo peak and have no any sharp diffraction

Table 1
O and N contents of the master alloy and the as-cast $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy rods with a diameter of 2 mm prepared in various atmospheres.

	Master alloy	Cast in Ar	Cast in N_2	Cast in air	Cast in O_2
O (wt.ppm)	7	4	5	26	18
N (wt.ppm)	4	5	9	7	8

peaks, implying the formation of amorphous phase without the existence of crystalline phases. The sample prepared in Ar has a D_{cr} of 2.5 mm, which is consistent with the previous reports [24]. However, just by replacing the casting atmosphere Ar with non-inert N_2, the D_{cr} quickly increases from 2.5 to 3.5 mm. Following, the $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ melt liquid was quenched in air, and the D_{cr} can still maintain 3.5 mm. This result also clearly suggests that O may not play a negative role in improving the GFA as previous reports arguing O would develop into heterogeneous nucleation sites of oxide and deteriorate the GFA [25,26]. Subsequently, we attempted to cast the $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ alloy liquid in pure O_2, an absolutely oxidizing atmosphere, and excitingly the D_{cr} could keep 3.5 mm. These results obviously indicate the O_2 has a same influence on improving the GFA as the N_2. Therefore, when the alloy was prepared in air, which can be regard as a mixture of N_2 and O_2, the D_{cr} remains. The fully amorphous nature of the 3.5 mm diameter rod prepared in O_2 atmosphere is further confirmed by the homogeneous contrast in the TEM image and the broad halo ring in the selected area electron diffraction (SAED) pattern, as shown in Fig. 2.

It was reported that different air pressures can trigger the variation of GFA and crystallization process of samples even though both the introduced O and N contents are ignorable [15]. Consequently, we examined the thermodynamic behaviors of all samples mentioned above carefully. Fig. 3 demonstrates the DSC heating curves of the $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ fully glassy rods with various diameters prepared in different atmospheres. It can be found no appreciable difference in T_g (=736.7 ± 0.5 K), T_x (=764.5 ± 0.3 K) or crystallization process is observed between the prepared-in-Ar sample and other glassy rods, suggesting the O or N elements don't impact the thermodynamic procedure and may be not introduced into the samples even cast in pure O_2 or pure N_2 atmospheres.

In order to determine the absorption of O and N in the master alloy as well as the glassy rods prepared in various casting atmospheres exactly, the O and N contents were measured by oxygen/nitrogen analyzer, as shown in Table 1. The order of O and N content is ppm (wt.), which is close to the previous reports [15,16]. The difference in O or N contents among these samples prepared in various atmospheres is negligible, suggesting that the O or N is not absorbed massively into the bulk alloy even cast in pure O_2 or pure N_2 atmosphere because of the short holding time. The result analyzed by oxygen/nitrogen analyzer and the DSC measurement verify each other in O or N aspect perfectly. Fig. 4 shows the hysteresis M-H curves of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy ribbons cast in Ar, N_2, air and O_2. It can be found that these samples display similar shapes and exhibit almost the same values of B_s and H_c. The glassy alloy exhibits excellent soft magnetic properties, its B_s is about 1.36 T and H_c is about 2.0 A/m, regardless of the applied casting atmosphere.

4. Discussion

Generally, once the preparation method is selected, for example copper mold casting, the alloy GFA mainly depends on the composition. However, in this paper, the results of O and N contents

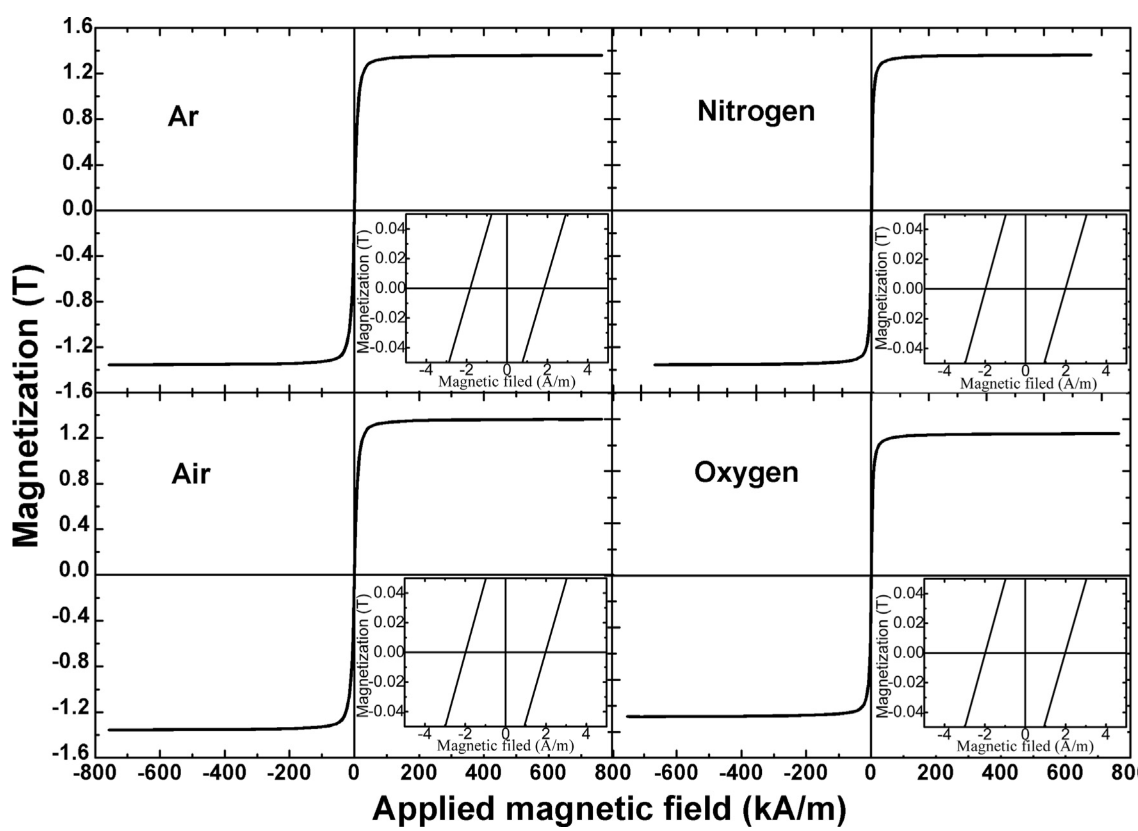

Fig. 4. Hysteresis M-H loops of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy ribbons prepared in Ar, N_2, air and O_2 atmospheres, respectively. The insets show the corresponding H_c.

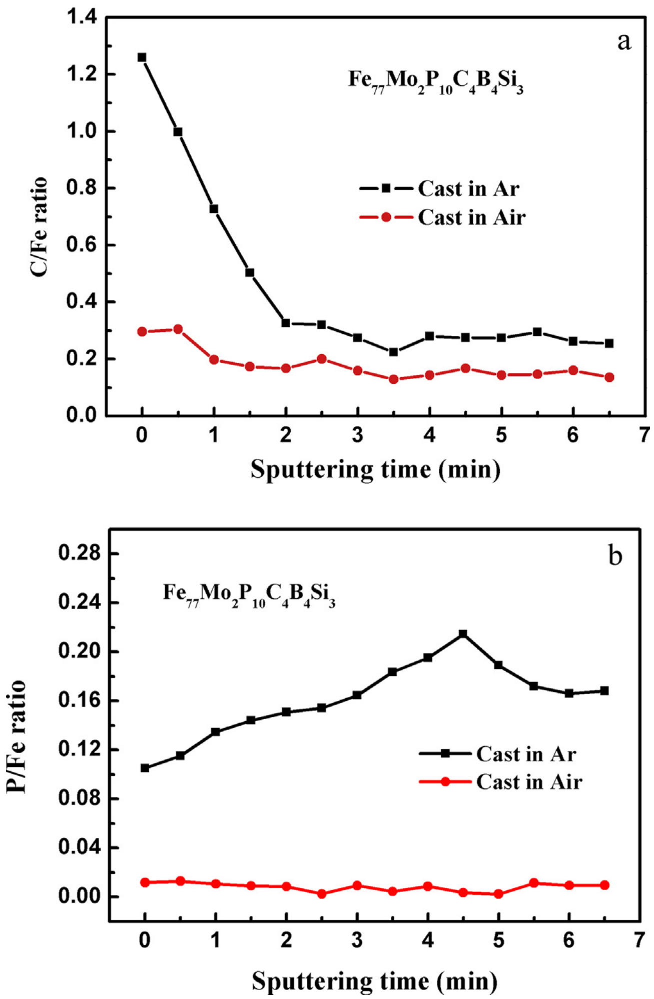

Fig. 5. (a) C/Fe, (b) P/Fe of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy alloys dependences of sputtering time.

measured by oxygen/nitrogen analyzer and DSC reveal the bulk composition does not vary with the species of the casting atmospheres. Hence, those composition-decided and GFA-related "whole bulk" thermodynamic properties or criteria, such as T_g, T_x, T_l, T_m, γ, etc., should not vary either, which has been proved by the DSC measurement in Fig. 3. When it seems the phenomenon could not be explained from "whole bulk" aspect, we try to make it from "surface" aspect. This trial is not totally groundless. During the preparation of the $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy alloy, the initating crystallization usually occurs on the edge rather than the center of the cross section, which is similar to the previous report in FeSiBPC alloy system [27]. Hence, it seems reasonable to deduce that the surface properties are involved with the GFA of the whole bulk alloy.

As is known, the heterogeneous nucleation rate can be defined as [1,19,20]:

$$I = AD\exp\left(-\frac{16\pi\sigma_{L-C}^3}{3kT(\Delta G_{L-C})^2}\right) \quad (1)$$

where, A is a constant, D the effective diffusivity, k the Boltzmann's constant, T the absolute temperature, ΔG_{L-C} the free energy difference between the liquid and crystal, and σ_{L-C} the liquid-crystalline interfacial tension. When the composition and T are fixed, D and ΔG_{L-C} remain the same as both of them are composition-determined. Here, it should be noted that surface tension is an important reflection of surface properties and very sensitive to the atmospheres, and it makes a small but noticeable contribution to the thermodynamic behavior of the whole system. During the solidification process of Fe-based alloy liquid, it is well-known some solute elements (e.g. C and P) are apt to be segregated into the free surface, while others (e.g. Mo, B and Si) remain evenly distributed in the "bulk" liquid. Therefore, the surface properties of the alloy should be carefully investigated.

The C and P distribution on the surface of glassy alloys cast in Ar and air atmospheres were examined through AES. In order to ensure the reliability of the data, the surface of sample was kept untouched and measured immediately after cast. It is assumed that the Fe content is constant during the data processing, and the dependence of other element-to-Fe ratio on the sputtering time is demonstrated in Fig. 5. From Fig. 5a, the C/Fe ratio is about 1.26 on the surface of the sample cast in Ar, which is much higher than the original ratio of $4/77(\approx 0.05)$. As the sputtering time went on, the C/Fe ratio dramatically reduce to a steady value of about 0.25, then drops slightly. However, for the sample cast in air, the C/Fe ratio is only 0.30 on the surface, and then gradually decreases to 0.15, which is still much larger than the original ratio. The C/Fe difference in the 2 atm means the C content close to surface is obviously dependent on the casting atmosphere species. When the alloy prepared in Ar, the P/Fe ratio is 0.11 on the surface, then rises and reaches to a maximum of 0.21, and afterward declines. In contrast, when prepared in air, surprisingly, the P/Fe ratio is almost constant and smaller than 0.01, which is much lower than the original ($10/77 \approx 0.13$), implying that oxidizing atmosphere has a strong effectiveness on eliminating P element. Additionally, it should be noticed that 1): concentration variations of C and P elements just occur on the liquid surface, and hardly happen in the "whole bulk", because the contact area of molten alloy liquid and atmosphere are limited and the holding time are short (about 5 s), causing the maintenance of whole bulk composition; 2) the difference of P/Fe ratio between the alloys prepared in Ar and air atmospheres is greater than that of C/Fe ratio, indicating that the species of casting atmospheres may play a more important role in changing P content than C content on the alloy surface.

Here, we discuss how the GFA of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ alloy depends on the species of casting atmosphere. It is possible for the N and O to dissolve in the $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ alloy. With the increasing of N or O contents, it was reported that the surface tension of liquid iron alloy would decrease because both N and O are surface-active elements [28]. Based on this result, according to Equation (1), the I would increase and GFA would deteriorate. That may be the reason why the preparation of Fe-based BMGs usually carries out in Ar atmosphere. However, firstly, in this work, as shown in Fig. 5, both the superficial P and C content of the samples prepared in air are lower that of alloys manufactured in Ar, respectively. It was reported that as the content of P or C element in iron alloy liquid declines, the surface tension will dramatically increase [29]. Therefore, the surface tension of alloy liquid melting in air should be larger than that of sample prepared under Ar, which would decrease the nucleation rate I and benefit the improvement of GFA [30]. When the increase effect of P and C on the surface tension triumph over the adverse impact of O_2 or N_2, the I will decrease and the GFA will be enhanced. Secondly, as O and N elements have a smaller atomic radius than the other original components [31], a small amount addition of O or N can change the composition as well as the thermodynamic properties on the surface of the molten alloy. It was reported that adding O or N could improve the atomic size differences and increase the element diversity of the alloy liquid [32–34]. Besides, the thermal enthalpies between the O and the Fe, Si, B, Mo, C and P constituent elements are about −824 kJ/mol, −910 kJ/mol, −1272 kJ/mol, −745 kJ/mol, −393 kJ/mol and −2984 kJ/mol, respectively. N also has negative heat of mixing with other original elements. The heat of mixing of N with the Fe, Si, B, Mo, C and P elements are −87 kJ/mol, −81 kJ/mol, −28 kJ/mol, −115 kJ/mol, −2 kJ/mol and −24.5 kJ/mol, respectively [31]. According to the Inoue's empirical rules, the increased element diversity, the atomic size mismatch and large negative heat of mixing would be conducive to the enhancement of GFA. It seems that the positive effect of O_2 and N_2 casting atmospheres on the GFA of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ glassy alloy can be attributed to the reduced nucleation rate caused by the enhancement of surface tension and the improvement of melt surface properties.

5. Conclusions

In this paper, the effect of different species of casting atmospheres on the GFA, composition and soft magnetic properties of $Fe_{77}Mo_2P_{10}C_4B_4Si_3$ bulk glassy alloy were investigated in detail. Our results show that proper non-inert casting atmospheres can enhance the GFA, while they do not impact upon the whole bulk composition as well as the soft magnetic properties. The unusual beneficial effect of non-inert atmospheres may be attributed to the reduced nucleation rate resulting from the enhancement of surface tension and the improved thermodynamic properties caused by the modified composition on the alloy surface. That might provide not only a novel method to improve the GFA of Fe-based BMGs without alloying any elements, but also a new thought to design composition of Fe-based BMGs utilizing casting atmospheres to increase GFA.

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