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Oxidation and refreshing behaviors of P-containing Fe-based amorphous ribbons

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ABSTRACT

Oxidation behaviors of $Fe_{78}B_{13}Si_{9-x}P_x$ (x = 0, 1, 3, 5 and 7) amorphous ribbons were investigated and a refreshing method by annealing in reductive atmosphere were successfully developed by considering the changes of magnetic properties and P content. It is found that the amorphous ribbons with high P content are prone to be oxidized at the beginning of a traditional annealing process. When the annealing process was under reductive atmosphere, however, not only the oxidation can be avoided but also the oxidized ribbon can be refreshed. It is found that, although the color is changed, the amorphous structure for both the oxidized and refreshed ribbons is not changed with the annealing conditions. The refreshing can recover the excellent soft magnetic properties of the alloys with P content lower than 5 at.%. The magnetization process characterized by magnetic domains has revealed the effect of refreshing ability to the oxidized ribbon. It is further confirmed that the refreshing mechanism of the oxidized layer is the valence state change of iron ions from high to low through the seriously oxidized $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon.

1. Introduction

Fe-based amorphous alloys possess excellent soft magnetic properties, including quite low coercivity (H_c), high permeability (μ_e) and low core loss, as compared to traditional silicon steel sheets [1–3]. These properties make them very attractive as magnetic core materials in distribution and other transformers, especially for high frequency power supplies. It has been reported that P addition can effectively improve the glass forming ability (GFA) of the alloys with high saturation magnetic flux density (B_s) and further extend their application fields [4–9]. However, the P introduction can also lead to a poor anti-oxidation of the Fe-based alloys and the occurrence of oxidation on the surface of the ribbons can severely affect the magnetic properties [10].In our previous work report [11], slight oxidation can further improve the magnetic properties for moderate P containing alloys. However, in most industrial production processes, a high vacuum annealing environment is not satisfied, therefore the alloy ribbon can be oxidized to some more serious extent during annealing [12]. Therefore, the soft magnetic properties are easy to be deteriorated due to the introduced magnetic anisotropy and pining centers, which was originated from the surface oxidation and such limit the promotion application of alloys [13]. To date, the effective method for solving oxidation of these glassy alloys has seldom been reported even some researchers have studied the effect of oxidation on the stability and magnetic properties of amorphous and nanocrystalline alloys [14–16].It is now quite common to see that H_2 atmosphere has been widely used for the reduction of hot-rolled strip [17], permalloy [18], and high phosphorus iron ore [19]. But the effect of H_2 atmosphere on the reduction of Fe-based amorphous alloy should be quite different from those applications due to its unique structure and characteristics. Hence, it will

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become a new topic for Fe based amorphous alloy annealed in reductive atmosphere to refresh the oxides formed on the surface of ribbon in industrial production. More importantly, the reductive atmosphere can prevent oxidation.

The aim of this work is to study the feasibility of the annealed P-containing Fe-based amorphous ribbons in H_2-Ar mixture atmosphere. Meanwhile, the effects of reduction atmosphere on oxidation inhibition and refreshing ability during the annealing process were studied. What's more, it is important to clarify the refreshing mechanism and effect on soft magnetic properties. Magnetic domain analyses were also carried out to reveal the different magnetization processes due to oxidation and refreshing on the ribbon surface. These results are meaningful for ameliorating the oxidation and promoting the application of Fe-based soft magnetic alloys.

2. Experiment procedures

Multi-component alloys with compositions of $Fe_{78}B_{13}Si_{9-x}P_x$ alloy (x = 0,1, 3, 5 and 7) were prepared by induction melting with the mixtures of pure Fe (99.99%), Si (99.99%), B (99.9%), pre-alloyed Fe_3P ingots under an argon atmosphere after the furnace was vacuumized to about 1×10^{-2} Pa. Ribbons with a width of about 1.3 mm and thickness of about 23–26 μm were prepared by single roller melt-spinning method at the wheel speed of 40 m/s in Ar atmosphere. The experiments were divided into three groups. First, ribbons were annealed in air or in H_2-Ar atmospheres at 673 K for 60 min as a controlled test. Second, the ribbons were exposed to dry air in an open-ended quartz-tube furnace at a temperature of 673 K for 10 min, and then were annealed in H_2-Ar (H_2 5 vol%) or in Ar atmospheres for 60 min. Third, the ribbons were annealed in H_2-Ar (H_2 5 vol%) atmosphere at 673 K for 70 min. The structures for the ribbons in different conditions were identified by X-ray diffraction (XRD, Bruker D8 Advance) with Cu*K*α radiation. As the magnetic properties depend on the size of the samples, ribbon samples with similar size about with a width of about 1.3 mm, thickness of about 23–26 μm and length of 75 mm were used for the measurements. Three samples were tested and an average value was obtained. The intrinsic magnetic properties including coercivity (H_c) and effective permeability (μ_e) at 40 Hz -1 MHz were measured using the $B-H$ loop tracer (EXPH-100) under the field of 800 A/m and the impedance analyzer (Agilent 4294 A) at 1 A/m, respectively. The magnetic domain structures of $Fe_{78}Si_9B_{13}$ and $Fe_{78}Si_4B_{13}P_5$ which annealed in air and H_2-Ar atmosphere at 673 K was characterized via the Magneto-optical Kerr Microscope. In addition, the evolution of the oxides formed on the surface of the $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon was characterized using the X-ray photoelectron spectroscopy (XPS, AXIS ULTRA) analysis. All the magnetic and XPS measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(a) shows the $Fe_{78}Si_4B_{13}P_5$ alloy ribbons produced with the industrial production and annealing lines which annealed in Ar atmosphere at 673 k for 90 min. The excellent surface quality and ductility of the as-spun ribbons manifest the attractive prospect of the P containing alloys. The obvious color change shows severe oxidation in the annealing furnace which is commonly used for $Fe_{78}Si_9B_{13}$ alloys. Similar phenomenon was also found in FeSiBPC, FePC, FeMoPCB alloy systems by our group, which will be reported elsewhere. Therefore it is necessary to develop a new annealing process to inhibit oxidation of the ribbon before it is put into used. Since the furnace chamber volume must be large for production line, under the condition of mechanical pump and the limitation of vacuumizing time, it is impossible to improve the vacuum degree. Therefore, the conventional annealing process protected by Ar atmosphere cannot prevent the amorphous ribbons to be oxidized.

To explore this problem, we have checked the effects of vacuum degree of the furnace in laboratory and the P content on oxidation, firstly. It was found that the oxidation layer formed fast when the vacuum degree is lower than 10^{-1} Pa for the alloys containing 5 at.% P [11]. Secondly, we annealed the alloys with different P content in air. It is found that the oxidized samples keep amorphous structure but they become more colorful (inset figure) with P content as shown in Fig. 1(b). It is clear that the anti-oxidation of the ribbons is decreased with the increase of P content. However, in a reduction atmosphere, i.e., annealing in H_2-Ar for 70 min, there is no much change for the color of the ribbons, which is shown in Fig. 1(c). It is interesting to find that even for oxidized samples, they can be refreshed without obviously color change as shown in Fig. 1(d). As identified by XRD, all the diffraction patterns show only one broad peak without any detectable sharp peaks, indicating the amorphous structure in all these alloys in different annealing conditions. It is hence concluded that annealing in reductive atmosphere can not only avoid but also refresh the undesirably oxidization of the annealed ribbons.

In order to consider the P content and refreshing effect of H_2-Ar atmosphere on the magnetic properties, the P content dependence of H_c for $Fe_{78}Si_{9-x}B_{13}P_x$ (x = 0, 1, 3, 5 and 7) amorphous ribbons, the $B-H$ loops, and the frequency dependence of effective permeability of $Fe_{78}B_{13}Si_6P_3$ ribbon annealed in the air for 60 min, air for 10 min and then H_2-Ar for 60 min, and air for 10 min and then Ar for 60 min at 673 K, respectively, were investigated, which are shown in Fig. 2.We can see from Fig. 2(a) that the H_c of $Fe_{78}Si_9B_{13}$ alloy remains the same low value after annealing in different conditions, implying a good anti-oxidation. With the increase of P addition, the deterioration of magnetic properties caused by oxidation becomes more and more serious after annealing in air. While the oxidation caused by 10 min annealing in air can be refreshed after annealing in H_2-Ar atmosphere, and the soft magnetic properties of the oxidized ribbons were greatly improved. Compared to Ar atmosphere, the sample annealed in H_2-Ar atmosphere can keep low H_c of about 1.4 A/m when P content is lower than 5 at.%. Further, It is found from Fig. 2(a) that the P content for the alloy should not be higher than 3 at.% when it is annealed in Ar atmosphere if it remains a relatively low H_c. Therefore, the ribbon with 3 at.% content, i.e., nominal composition of $Fe_{78}Si_6B_{13}P_3$ alloy was used to give further magnetic information. Fig. 2(b) shows the typical $B-H$ loops of $Fe_{78}Si_6B_{13}P_3$ alloys under different annealing atmospheres. We found that the narrow loop with the lowest H_c is the ribbon annealed in H_2-Ar atmosphere. As the effective permeability (μ_e) of the annealed ribbons under different frequency is an important parameter in terms of their industrial applications [20,21], the frequency dependence of μ_e for the $Fe_{78}Si_6B_{13}P_3$ amorphous alloy was measured under applied magnetic field (H_m) of 1 A/m. As shown in Fig. 2(c), the μ_e keeps same value of about 9600 whether the ribbons annealed in Ar or H_2-Ar atmospheres, while the value of about 5200 was obtained after annealing in air at 900 Hz. The result is consisted with result of H_c. All μ_e curves maintain stable frequency characteristics, and high cut-off frequencies of about 40 kHz.

In order to reveal the effect of oxidized surface of P-containing ribbons on the soft magnetic properties, the magnetic domains of the representative $Fe_{78}Si_9B_{13}$ and $Fe_{78}Si_4B_{13}P_5$ ribbon samples annealed in different atmospheres were studied by using Magneto-optical Kerr Microscopy, which is shown in Fig. 3. Since the samples subjected to long time oxidation were covered with thick oxidation layer which was found to result in less obvious contract in magnetic domain pattern, we chose the samples annealed for 10 min in air to give a clear illustration. When the annealing below the crystallization temperature, structural relaxation will lead to a more uniform microstructure. At the same time, stress release and free volume annihilating happen, which results in regular patterns of the domains for alloy without P addition, because there was no obviously oxidation on the surface even annealed in air atmosphere. However, domain morphologies cannot be clearly observed forFe$_{78}$Si$_4$B$_{13}$P$_5$ alloys annealed in air due to the existence of oxidized layer. The oxides can cause tensile stress in the amorphous

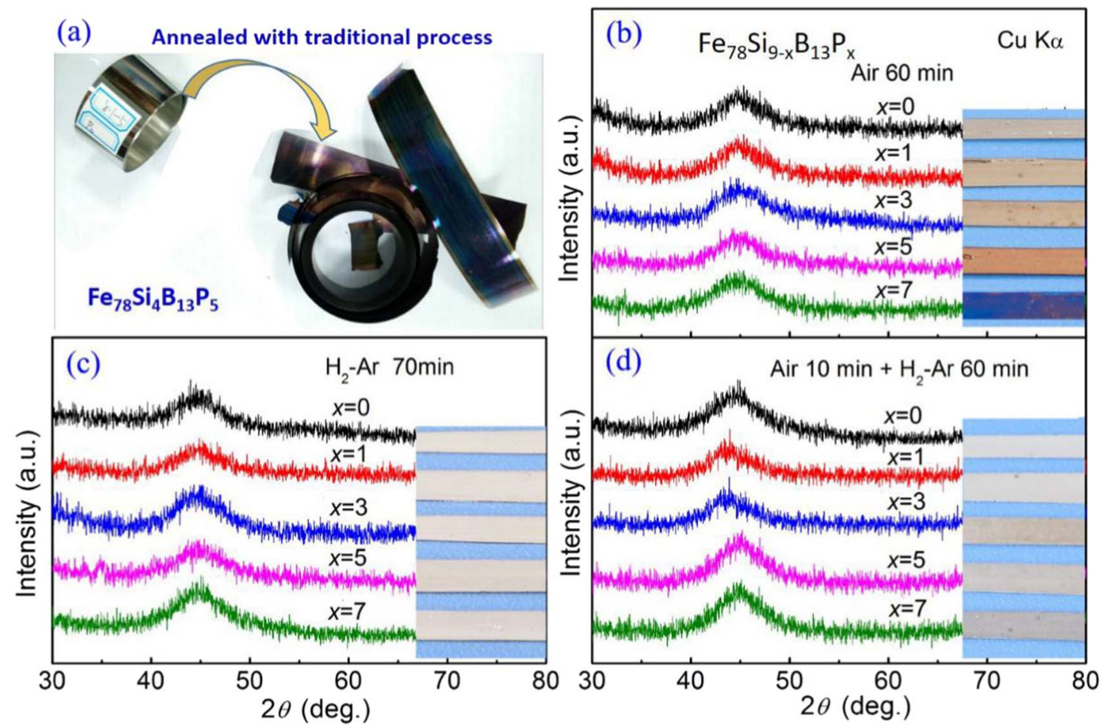

Fig. 1. Photos of the ribbons (a) and XRD patterns of the $Fe_{78}B_{13}Si_{9-x}P_x$ (x = 0, 1, 3, 5 and 7) alloy ribbons under annealing conditions of air for 60 min (b), H_2-Ar for 70 min (c), and air firstly for 10min and then refreshed in H_2-Ar for 60 min (d). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

matrix [22], which is the source of pinning centers to restrict the domains formation and deteriorate the soft magnetic properties. After annealing in H_2-Ar atmosphere, the oxidized layer was refreshed and the magnetic domains can be clearly observed again. Which is consistent with the results shown in Fig. 1(d) that the reductive atmosphere can effectively refresh the oxidized surface.

To further understanding the mechanism of reductive atmosphere on the improvement of soft magnetic properties and build the connection between magnetic domain structure and oxidation, XPS analysis was performed to characterize the evolution of the oxides formed on the surface of the $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon, i.e., the easiest one to be oxidized in air atmosphere. The peaks of electronic configuration for Fe 2p, Si 2p, and O 1s were investigated (not shown here).Here we show the related spectra of Fe 2p in Fig. 4. The spectra are normalized to the same height at their maximum peaks and moved up and down as necessary. The as spun ribbon has a homogeneous chemical composition which can supply silicon to build up a thin layer of SiO over the whole surface of ribbon when it is annealed in air. At the same time, iron oxide nucleates and grows within the thin SiO film. The Fe2p spectrum is corresponding to the peaks of Fe 2p1/2 and 2p3/2 including the peaks of the metallic state (Fe^m), i.e., Fe^{2+} and Fe^{3+} as well as oxide states (Fe^{ox}) [23]. It has been shown [24] that the peak positions of Fe 2p1/2 and Fe 2p3/2represent the total angular momentum quantum number which depends on the ionic states of Fe. In

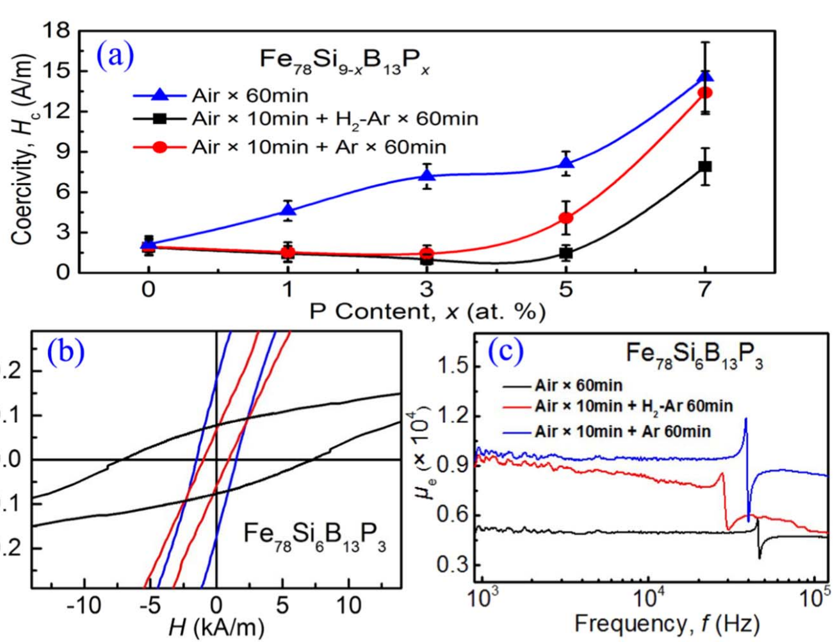

Fig. 2. (a) P content dependence of Hc for $Fe_{78}Si_{9-x}B_{13}P_x$ (x = 0, 1, 3, 5 and 7) amorphous alloys annealed in the air, H_2-Ar and Ar atmospheres at 673 K, respectively; (b) B—H loops and (c) Frequency dependence of effective permeability of $Fe_{78}B_{13}Si_6P_3$ amorphous ribbon.

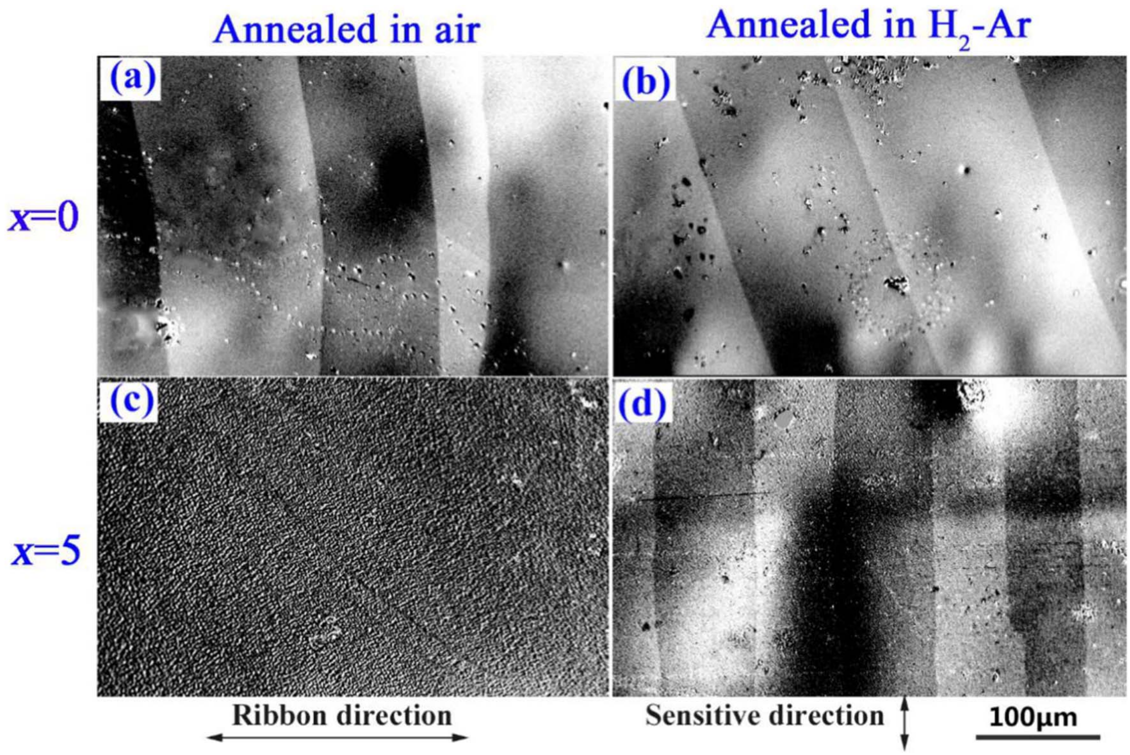

Fig. 3. Typical magnetic domain patterns of $Fe_{78}Si_9B_{13}$ ribbons annealed in air (a) and in H_2 + Ar (b), respectively, for 60 min, and $Fe_{78}Si_4B_{13}P_5$ amorphous ribbons annealed firstly in air for 10 min (c) and then in H_2 + Ar for 60 min (d), at 673 K, respectively.

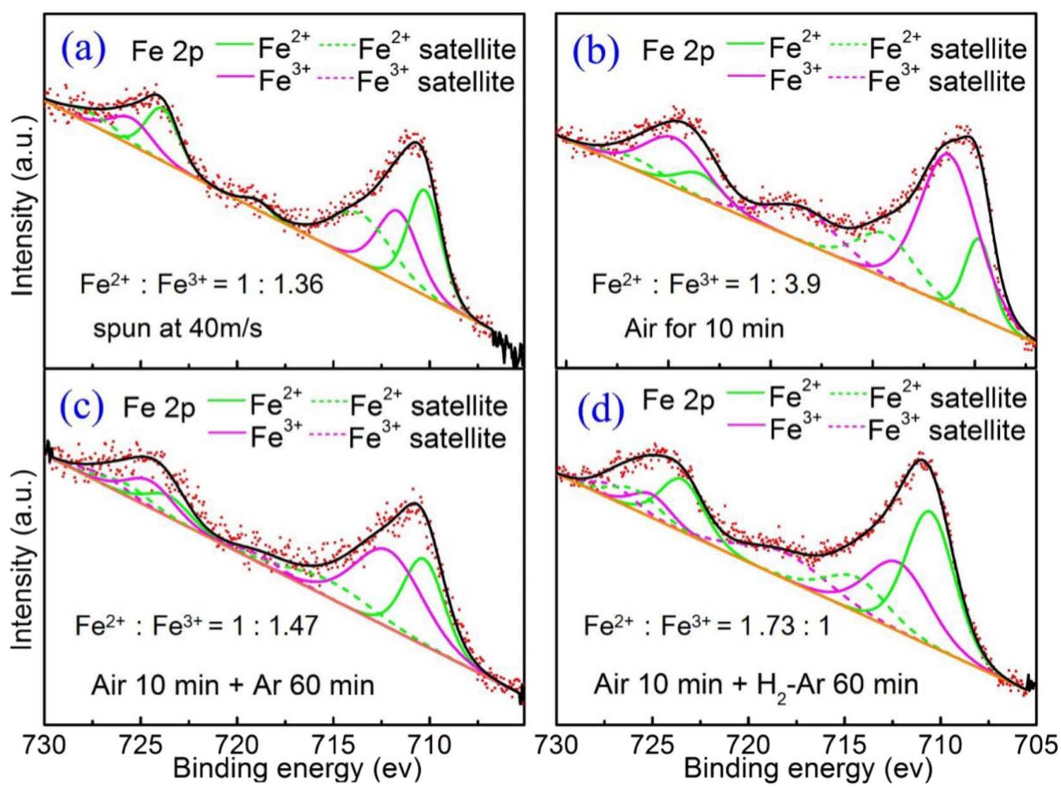

Fig. 4. XPS spectra of Fe 2p for $Fe_{78}Si_2B_{13}P_7$ alloy ribbons in as-spun (a), as-annealed (in air for 10 min (b), in air for 10 min and then in Ar for 60 min (c), in air for 10 min and then in H_2 + Ar for 60 min, respectively) states.

addition, two satellite peaks occur at about 8 eV (Fe^{3+}) and6 eV (Fe^{2+}), indicating a higher binding energy than the main Fe 2p peaks. According to the binding energy, the intensity of main peak and the basic data reference of XPS, Fe_3O_4, Fe_2O_3 and FeO can be distinguished in the graphs. The area ratio of each peak represents the proportion of Fe^{2+} and Fe^{3+}. Fig. 4(b) shows XPS results about ribbons annealed in air for 10 min, more Fe^{3+} than Fe^{2+} can be seen and much Fe_2O_3 formed on the surface causing the decrease of soft magnetic properties when it is compared to results obtained in Fig. 4(a). However, the ratios of Fe^{2+} to Fe^{3+} decrease indicating that more and more Fe^{3+} was refreshed to Fe^{2+} when the ribbons annealed in Ar (Fig. 4(c)) and H_2-Ar (Fig. 4(d)) protective atmospheres. Therefore, more and more $Fe_3O_4$is formed and soft magnetic properties of material can be improved.

In this paper, we firstly have explored the refreshed effect of reductive atmosphere on oxides, magnetic domain structure and magnetic properties of the amorphous ribbons. Due to their chemical homogeneity and the absence of the grain boundaries, it is predicted that the oxidation of the amorphous alloys is more uniform compared to that of crystalline iron alloy. According to the report given by Hennayaka [25], the thickness of the oxide layer is extremely small. So it cannot be characterize by XRD, and all alloys are amorphous as shown in Fig. 1. However, the pining effect caused by oxides can deteriorate the soft magnetic properties. What's more with the increase of P, the density of the oxide increases. However, the oxidized surface can be refreshed after annealing in H_2-Ar atmosphere, which is proved by the results of magnetic domain tests as shown in Fig. 3. Compared to the Ar atmosphere, H_2-Ar atmosphere not only has the ability to isolate oxygen to contact with the ribbons but also reduce oxides on the ribbon surface. While Ar atmosphere has relatively weak ability to reduce oxides, therefore the oxidized layer formed at the first 10 min during annealing stage cannot be totally refreshed for the ribbons with P content higher than 5 at.%.

Then we discuss the mechanism of enhanced magnetic properties and the change of the surface oxides through $Fe_{78}Si_2B_{13}P_7$ alloy ribbons, the one of seriously oxidized. The mechanism of the reaction for the reduction of iron oxides on the ribbon surface varies with temperature. XPS investigations show the reduction route of oxides formed on the surface of $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon can be described as the valence state change of iron ions from high to low when reduction temperature is lower than 770 K [19]:

$$Fe_2O_3 \rightarrow Fe_3O_4$$

The different amount of Fe_3O_4 formation caused by different annealing processes shown in Fig. 2(a) is the results of the difference in H_c value due to the known magnetic properties of Fe_3O_4 [19]. The lowest H_c value for $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon annealed in H_2-Ar atmosphere demonstrates that the refreshing method we developed is helpful in development of P-containing Fe-based amorphous ribbons as a new kind of soft magnetic materials.

4. Conclusion

The feasibility and soft magnetic properties of annealed P-containing Fe-based amorphous ribbons in reduction atmosphere were examined in detail. We provide a new method to refresh the oxidized ribbons successfully in reduction atmosphere during the annealing processes. It has great effect on promoting the application of Fe based amorphous ribbons. The main conclusions are as follows:

1. The H_2-Ar atmosphere has a significant reduction effect on $Fe_{78}B_{13}Si_{9-x}P_x$ (x = 0–7) amorphous alloys. The reductive ability is restricted by P content, i.e., when P content is lower than 5 at.%. The ribbon presents a lower H_c as compared to the ribbon annealed in other atmospheres. While the P content should not be higher than 3 at.% for the ribbon annealed in Ar atmosphere.
2. The soft magnetic properties of P-containing alloys were improved including low H_c of about 1.4 A/m, high stable μ_e of about 9600 after annealing in H_2-Ar atmosphere. The magnetic properties were improved obviously with P content not less than 3 at.%.
3. The mechanism of the refreshing is the change of Fe^{2+} into Fe^{3+} and formation of Fe_3O_4 on the surface of $Fe_{78}Si_2B_{13}P_7$ amorphous ribbon, resulting in the improvement of the magnetic properties of the material investigated.

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