

# Effect of Y and B content tailoring on the crystallization behavior and corrosion resistance of Fe<sub>76-2x</sub>Y<sub>4+x</sub>B<sub>20+x</sub>(x=0 and 2) glassy alloys

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**Abstract.** The effect of Y and B content tailoring on the crystallization behavior and corrosion resistance of Fe<sub>76-2x</sub>Y<sub>4+x</sub>B<sub>20+x</sub>(x=0 and 2) glassy alloys have been investigated. The tailoring of yttrium and born content enhances the thermal stability of x=2 alloy, alters the crystalline mode from a two-stage of x=0 glassy alloy to a three-stage of x=2 glassy alloy. Crystallization deteriorates the corrosion resistance of x=2 glassy alloy in alkaline solution. With increase annealing time from 5 to 30 min, the corrosion potential and its corresponding lattice constant of  $\alpha$ -Fe phase of x=2 alloy show a similar change, the result is related to the change of solute atom composition in  $\alpha$ -Fe grain in the local galvanic cell reaction.

## Introduction

Recently, the new ternary Fe-Y-B glassy alloys are fabricated which possess high glass forming ability (GFA) and excellent soft magnetic properties as compared with the binary Fe-B amorphous alloys [1,2]. The simple phase component of Fe-Y-B glassy system makes it an attractive base alloy for developing new Fe-based nanocrystalline alloy [3]. In this work, we aim at investigate the evolution of local atomic structure via minor alloying of Y/B in crystallization, as well as the effect of the crystallization behavior on the corrosion resistance of  $Fe_{76-2x}Y_{4+x}B_{20+x}(x=0 \text{ and } 2)$  glassy alloys. This basic scientific research may contribute to developing a new Fe-Y-B based dual-phase nanocrystalline/glassy alloy.

# **Experimental procedures**

Ingots with nominal compositions of  $Fe_{76-2x}Y_{4+x}B_{20+x}(x=0 \text{ and } 2)$  (at. %) were prepared by arc melting. The ingots were inductively heated in quartz tube and spun by using a single copper roller in argon atmosphere. The obtained ribbons were 20-50 µm in thickness and 2-3 mm in width [4]. The isothermal heat treatments were carried out at 873K and 923K and holding for various times under argon atmosphere. Specimens were investigated by the X-ray diffraction (XRD, Cu K $\alpha$ ,  $\lambda$ =0.15405 nm), FEI Tecnai F30 transmission electronic microscopy (TEM) and differential scanning calorimeter (DSC, Netzsch404). Electrochemical measurement was carried out by using a typical three-electrode system containing a working electrode, a platinum counter electrode and an Hg|Hg2Cl2 (SCE) reference electrode.

# Results

Fig. 1 shows the XRD patterns and of  $Fe_{76-2x}Y_{4+x}B_{20+x}(x=0 \text{ and } 2)$  glassy ribbons after annealing at 873K and 923K, respectively, annealing times ( $t_A$ ) are set as 5, 10, 30 and 60 min, respectively. As shown, x=0 ribbon for  $t_A=5$ , 10, 30 and 60 min show the same precipitated phases which are mainly  $\alpha$ -Fe and Fe<sub>3.5</sub>B, indicating that the x=0 glassy ribbon from thermally destabilization to its equilibrium state is in less than 5 min. For x=2 ribbon, it can be seen that the amount of the precipitated Fe-B compounds increase with increasing tA from 5 min to 30 min. The precipitated



phases of  $t_A=30$  min are the same as those of  $t_A=60$  min. The same precipitated phases in  $t_A=30$  and 60 min demonstrate that x=2 ribbon from thermally destabilization to its equilibrium state is in less than 30 min, which is more slow than that of x=0 ribbon. The sluggish  $t_A$  of x=2 ribbon suggests that it has a higher thermal stability than x=0 ribbon in supercooled liquid region.



**Fig.1.** XRD patterns of  $Fe_{76-2x}Y_{4+x}B_{20+x}(x=0 \text{ and } 2)$  glassy alloys annealed at 873K and 923K holding for various times, respectively: (a) x=0 alloy; (b) x=2 alloy; (c)  $C_p$  curves of x=0 and 2 glassy ribbons.

Fig. 2 shows the high resolution TEM (HRTEM) micrograph of x=2 ribbon in amorphous state. The HRTEM micrograph shows some ordered regions whose sizes are less than 1 nm. The lattice-fringe spacing of these ordered regions are 0.219 nm, corresponding to the lattice spacing of (422)<sub>Fe23B6</sub>. It is reported that the metastable Fe<sub>23</sub>B<sub>6</sub> phase is composed of symmetrically arrangement Archimedean antiprism (AAP), and AAP is a twisted form of tri-capped triangular prism [5]. According to the nanoscale phase separation model [6], these ordered regions with AAP medium-range order (MRO) microstructure are actually structural fluctuations existing in the alloy, which could act as the nuclei of primary Fe<sub>23</sub>B<sub>6</sub> phase in crystallization. Hence, combining with the change of crystallization mode and the higher thermal stability, we can conclude that the tailoring of Y/B content enhances the geometrical frustration of x=2 glassy ribbon and leads to a high diffusion difficulty of atoms in the nucleation and growth process of the competing primary crystalline phase [5].



**Fig.2.** High resolution TEM (HRTEM) morphology of x=2 glassy ribbon, insets are enlarged images corresponding to squares I and II.

Fig. 3 shows the potentiodynamic polarization curves of x=2 glassy ribbon after annealing for 5, 10, 30 and 60 min at 923K in 0.1 mol/L NaOH solution. The polarization curve of as-spun x=2 ribbon is shown for comparison. The vertical increase of the current density in anodic reaction means that x=2 ribbon for  $t_A=60$  min has a worst corrosion resistance among all the measured ribbons. On the contrary, as-spun ribbon shows a lowest  $i_{pass}$  and most positive  $E_{corr}$ , and possesses the best corrosion resistance. It can be seen that ribbons for  $t_A=5$ , 10 and 30 min show three anodic activation peaks (denoted by arrows in Fig.4, labeled as  $A'_{p1}$ ,  $A'_{p2}$  and  $A'_{p3}$ ) in the passive regions. According to the earlier works [7],  $A'_{p1}$ ,  $A'_{p2}$  and  $A'_{p3}$  correspond to the dissolution of  $\alpha$ -Fe, metastable Fe<sub>3</sub>B and stable Fe-B compounds (Fe<sub>2</sub>B or FeB). As shown,  $A'_{p1}$  shows the highest current density and lowest  $E_{corr}$  compared with  $A'_{p2}$  and  $A'_{p3}$ , suggesting that the dissolution of  $\alpha$ -Fe phase dominated the polarization reaction of present Fe-based dual-phase alloys. The  $E_{corr}$  and  $i_{pass}$  deduced from Fig. 3 are listed in table 1, and the plot of  $E_{corr}$  vs.  $t_A$  is shown in Fig. 4b. Based on  $E_{corr}$  and  $i_{pass}$  results, we can conclude



that the order of the corrosion resistance in alkaline solution is as follows: as-spun >  $5 \min > 30 \min > 10 \min > 60 \min$ .



Fig.3. Potentiodynamic polarization	curves of $x=2$	ribbon after	annealed t	for various	times at	923K in
	0.1 mol/L Na	OH solutior	1.			

Table 1 Corrosion potentials ( $E_{corr}$ ) and passive current densities ( $i_{pass}$ ) deduced from polarization
curves of $x=2$ ribbon after annealed for various times at 923K in 0.1 mol/L NaOH solution.

Alloys	$t_{\rm A}({\rm min})$	$E_{\rm corr}({ m V})$	$i_{\text{pass}}(\text{A/cm}^2)$
$Fe_{72}Y_6B_{22}$ (x= 2)	As-spun	-0.53	$1.8 \sim 4.6 \times 10^{-9}$
	5min	-0.74	4.6~8.17×10 <sup>-9</sup>
	10min	-0.86	$2.52 \sim 12.5 \times 10^{-7}$
	30min	-0.81	$1.91 \sim 25.2 \times 10^{-8}$
	60min	0.72	

Fig. 4 shows plots of various parameters deduced from XRD and polarization curves of x=2 ribbons as a function of  $t_A$ . The peak position 2q and lattice constant  $a_0$  of  $\alpha$ -Fe deduced from (110) peaks in XRD curves vs.  $t_A$  are shown in Fig. 4a.  $a_0$  was calculated using *Scherrer* equation. With increasing  $t_A$ ,  $a_0$  first decrease and then increase flat, the maximum value is at  $t_A=10$  min, while 2q values show an inverse trend. Interestingly, when  $t_A$  increase from 5 to 30 min, the variation of  $E_{corr}$  is similar to  $a_0$ . From  $a_0$  and  $E_{corr}$  curves, it could be seen clearly that there exist a transition at  $t_A=10$  min, suggesting that a new crystallization reaction has happened at  $t_A=10$  min in the crystallization process of x=2glassy alloy.



**Fig.4.** (a) plots of the (110) peak position and lattice constant  $a_0$  of  $\alpha$ -Fe as a function of annealing times ( $t_A$ ); (b) corrosion potentials ( $E_{corr}$ ) vs.  $t_A = 5$ , 10 and 30 min.

## Discussions

## crystallization behavior of Fe<sub>76-2x</sub>Y<sub>4+x</sub>B<sub>20+x</sub>(x=0 and 2) glassy alloys

According to Hono's work and above discussions [8], there are two types of precipitated  $\alpha$ -Fe phase in the isothermal annealed *x*=2 alloy, one is decomposed by primary Fe<sub>23</sub>B<sub>6</sub> phase with a large grain size (labeled as  $\alpha_I$ ), the other is decomposed by the amorphous matrix with a small grain size (labeled as  $\alpha_{II}$ ) [9].

Hence, we can explain the relation between the crystallization reaction and precipitated phases existing in XRD patterns of x=2 alloys based on the above discussion. For  $t_A=5$  min, the dominated



reaction is the decomposition of Fe<sub>23</sub>B<sub>6</sub> phase, the precipitated phases are mainly  $\alpha_I$  phase and small amount of Fe-B compounds. When  $t_A$  increase from 5 to 10 min, the decomposition of Fe<sub>23</sub>B<sub>6</sub> phase has finished while decomposition of Fe-B matrix just start. In these two stages,  $\alpha_I$  phase grow up along with the solute elements Y and B ejecting out and segregating in the remaining amorphous matrix, which causes *D* increasing and  $a_0$  decreasing [1]. Thus, the transitions in  $a_0$  and *D* curves are in fact the start of Fe-B matrix decomposition. When  $t_A$  increase from 10 to 60 min, the Fe-B matrix has decomposed, the eutectic  $\alpha_{II}$  and metastable Fe-B compounds precipitate and grow up. The segregation of the solute elements in the remaining matrix in previous stage leads to lattice constant of eutectic  $\alpha_{II}$  phase increasing, accordingly, causes an flat increasing of  $a_0$  (here,  $a_0$  is mean value of  $\alpha_I$ and  $\alpha_{II}$ ). Therefore, the change of  $a_0$  actually reflects the change of Y/B concentration in  $\alpha$ -Fe phase, especially Y concentration in  $\alpha$ -Fe phase.

#### Effect of crystallization on the corrosion resistance behavior of Fe72Y6B22 glassy alloys

It has been reported that ferric and yttrium oxide films play a major protective role during the corrosion process of Fe-Y-B glassy alloys, hence, the passive regions in the anodic polarization curves of the present alloys are due to the formation of yttrium oxide film on the surface [10]. The formation of the dual-phase nanocrystalline structure in the present alloys could give rise to a galvanic cell reaction in present alkaline solution [7]. Moreover, as the predominant precipitated phases in x=2 glassy alloy for  $t_A=5$ , 10 and 30 min are  $\alpha$ -Fe, the anode and cathode in present local galvanic cell reactions are  $\alpha$ -Fe and the amorphous matrix, respectively. Hence, the anodic polarization behavior of the present dual-phase alloys is dictated by the chemical composition of the  $\alpha$ -Fe phase, i.e. the higher the Y concentration in  $\alpha$ -Fe phase, the thicker and more continuous passive film on the surface [7]. Hence, we can understand the similar trend between  $a_0$  and  $E_{corr}$  of x=2 alloy for  $t_A$  from 5 to 30 min.

#### Conclusions

The crystallization behavior and corrosion resistance of  $Fe_{76-2x}Y_{4+x}B_{20+x}(x=0 \text{ and } 2)$  glassy alloys have been investigated, reaching the following new conclusions:

1. The tailoring of Y/B content enhances the thermal stability and corrosion resistance properties of x=2 glassy alloy, and change the crystalline mode from a two-stage mode of x=0 alloy to a three-stage mode of x=2 alloy.

2. Crystallization deteriorates the corrosion resistance of x=2 glassy alloy.  $a_0$  of  $\alpha$ -Fe phase and  $E_{corr}$  of x=2 glassy alloy after annealing for 5, 10 and 30 min show a similar change.

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