

Effect of Au Addition on Intermetallics Precipitation Tendency and Repassivation of $\text{Al}_{88}\text{Fe}_5\text{Y}_7$ Glassy Alloy

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The effects of Au addition and annealing on selective intermetallics precipitation and corrosion behaviors of the as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys have been investigated. When Au content $x = 0$, the alloy has more preferentially precipitated AlY phase, the larger ΔE ($= E_p - E_{\text{prot}}$, E_p and E_{prot} are pitting and protective potentials) in Tafel curve, and the higher steepness k_s ($= dE/d\log(I)$) on the reverse scan, suggesting that there exist some tunnels in the pit interiors and the repassivation can be hindered; whereas in case of $x = 0.5$ and 1 , the AlFe phase precipitates more easily, and the ΔE and k_s of the alloys are lower obviously. The repassivation and pitting transition of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy alloys are closely associated with the intermetallics precipitation tendency and fraction of amorphous phase.

Keywords: intermetallics selection; passivation; pitting transition; steepness; tunnel

1. INTRODUCTION

Al-based glassy alloys with aluminum content over 80 at.%, especially Al-TM (Fe, Co and Ni: 1–15 at.%)–RE (Y, Gd and Ce: 3–20 at.%) alloys exhibit excellent corrosion resistance, good ductility and other mechanical properties [1-5]. Due to the remarkable glass forming ability (GFA), $\text{Al}_{88}\text{Fe}_5\text{Y}_7$ glassy alloy has been extensively studied in the last decade. Its atomic structure, crystallization scheme and effects of microalloying on glass formation have been deeply investigated [6-9]. It is known that minor elemental addition can effectively enhance thermal stability or alter corrosion behavior of the glassy alloys, owing to changing the enthalpy of mixing (ΔH_{mix}) [10], average atomic packing

efficiency (ε) [11] and electronic structure effect by adding some solute elements [12]. However, there is little work on the corrosion resistance of the $\text{Al}_{88}\text{Fe}_5\text{Y}_7$ alloy with microalloying technology.

Although Al-based amorphous alloy has the highly corrosion resistance because of the chemical and structural homogeneity [13, 14], the pitting corrosion induced by chloride ion in sea water environment happen easily and cause the premature failure of materials. Therefore, it is great meaningful to research the pitting corrosion and repassivation phenomenon of Al-based amorphous alloy. Two potential parameters which are determined from the potentiodynamic cyclic polarization curves, the pitting potential (E_p) and the protection potential (E_{prot}) can well be used to evaluate the pitting corrosion resistance of samples [14, 15]. Moreover, the pit transition phenomenon in the repassivation process of some samples on the reverse scan often arises. There are a few interpretations about this behavior of aluminium. Nisancioglu and Holtan [16] attributed this behaviour which occurred at the pitting region to crystallographic corrosion. Yasuda et al. [17] linked the transition phenomenon to the lateral undermining of deeper pits. Newman et al. [18] suggested that there has a tunnel in the bottom of pits, which may be the cause of a transition. However, the factors and mechanism of the pitting transition and repassivation of glassy alloy are still unclear. In this work, we used the $\text{Al}_{88}\text{Fe}_5\text{Y}_7$ alloy as the start alloy and selected Au as the additional element to investigate the effect of Au addition on the glass formation and pit transition in the repassivation of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy alloys. We try to explain the selective intermetallic phase precipitation with the average atomic packing efficiency, the mixing enthalpy and mismatch entropy and the effects of adding Au element on pitting transition phenomenon in $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys. In addition, in order to comprehensively understand the pitting transition, we also researched the corrosion behavior of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ nanocrystalline and fully crystallized alloy ribbons.

2. EXPERIMENTAL

The alloy ingots of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) were prepared by induction-melting the mixture of pure Al (99.9 wt %), Fe (99.7 wt %), Y (99.5 wt %), Au (99.5 wt %) ingots in a high-purity argon atmosphere. The glassy ribbons of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) were obtained by a single roller melt-spinning technique in argon atmosphere with the circumferential speeds of 25.6 m/s. The samples are about 30 μm in thickness and 1-3 mm in width. $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ ribbon was isothermally annealed using the annealing furnace in a high-purity argon atmosphere.

The structures of the master alloys, as-spun and as-annealed specimens were investigated by an X-ray diffractometer (XRD, Rigaku D/max-rB) with Cu Ka radiation. Otherwise, the structure of the $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-annealed alloys was also investigated by transmission electron microscopy (Tecnai 20U-TWIN). Here, samples were investigated for TEM by ion jet thinning until a hole was created. The thermal properties of the as-spun samples were investigated by differential scanning calorimetry (DSC, Netzsch DSC 404) under an argon atmosphere at a heating and cooling rate of 20 K/min.

Electrochemical measurements of the master alloys, as-spun and as-annealed samples were carried out on a CHI660E electrochemical workstation in 3.5 wt.% NaCl solution at room temperature and used a typical three-electrode system: working electrode, platinum counter electrode and

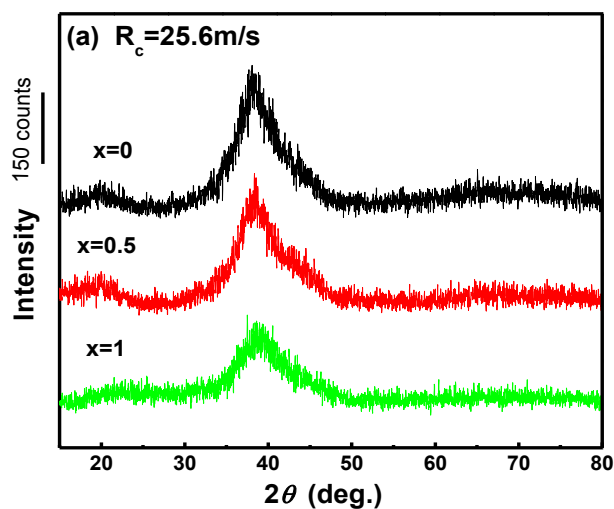
Hg|Hg₂Cl₂ (SCE) reference electrode. The single potentiodynamic cyclic polarization curves were obtained at a scan rate of 1 mV/s after holding the samples at the open circuit potential for 10 minutes. The ethanol and deionized water were used to clean the corroded ribbons. All the single potentiodynamic cyclic polarization curves were measured at room temperature and repeated at least three times. The corrosion morphologies of the ribbons after polarization experiments were examined by scanning electron microscopy (SEM, Hitachi SU-70). In addition, the chemical compositions of the corresponding corrosion regions were determined by energy dispersive spectroscopy (EDS). The surface films of the corroded samples were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250) performed on photoelectron spectrometer with Al-K α excitation.

3. RESULTS

3.1 As-spun Al_{88-x}Fe₅Y₇Au_x ($x = 0, 0.5$ and 1) alloys and master alloys

3.1.1 XRD patterns of as-spun Al_{88-x}Fe₅Y₇Au_x ($x = 0, 0.5$ and 1) alloys and their master alloys

Fig. 1 shows the XRD patterns of as-spun Al_{88-x}Fe₅Y₇Au_x ($x = 0, 0.5$ and 1) samples with a spinning speed R_c of 25.6 m/s and their master alloys. Obviously, there is a typical broad diffraction peak centered at $2\theta = 35^\circ \sim 45^\circ$ in the XRD patterns of three as-spun ribbons, suggesting that the samples at this speed have a fully amorphous structure. There are completely crystallized phases in the master alloys, we denote their spinning rate $R_c = 0$ in this paper. In case of $x = 0$, the major diffraction peaks are corresponding to α -Al, Al₃Y, Al_{3.25}Fe and Fe₂Y phases. In case of $x = 0.5$ and 1 , crystalline phases Al₅Fe₂ and Al₂Au appear, and the amount of Al₃Y decreases (Fig. 1b), indicating that the addition of Au can promote the precipitation of Al₅Fe₂ phase.



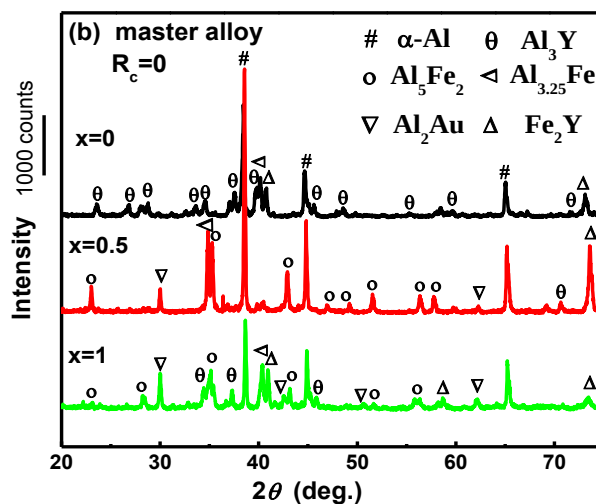
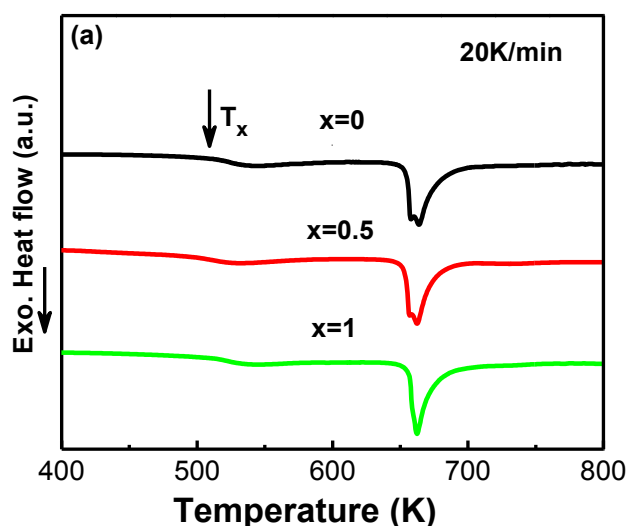


Figure 1. XRD patterns of the (a) as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) samples at spinning speeds R_c of 25.6 m/s and (b) master alloys ($R_c = 0$).

3.1.2 Thermodynamic behavior of as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy alloys

Fig. 2 illustrates the DSC curves of as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) ribbons with $R_c = 25.6 \text{ m/s}$ under the heating and cooling rates of 20 K/min . In the heating range from 400 to 800 K , two detached exothermic peaks correspond to two-step crystallization mode of the as-spun glassy alloys. The first exothermic peak is related to the primary crystallization of nanocrystalline $\alpha\text{-Al}$ and the second one results from the eutectic crystallization of residual amorphous phase [9]. In the heating range from 800 to 1173 K , there is one major endothermic peak together with an obscured shoulder peak, suggesting the eutectic and primary melting processes, respectively. During the cooling process, there are one major exothermic peak and an obscured exothermic peak, with a super cooling degree of $20\text{-}50 \text{ K}$ compared with the melting process. Especially, there are three sub-peaks overlapped in the eutectic exothermic peaks, and the highest sub-peak shifts towards low temperature with increasing x .



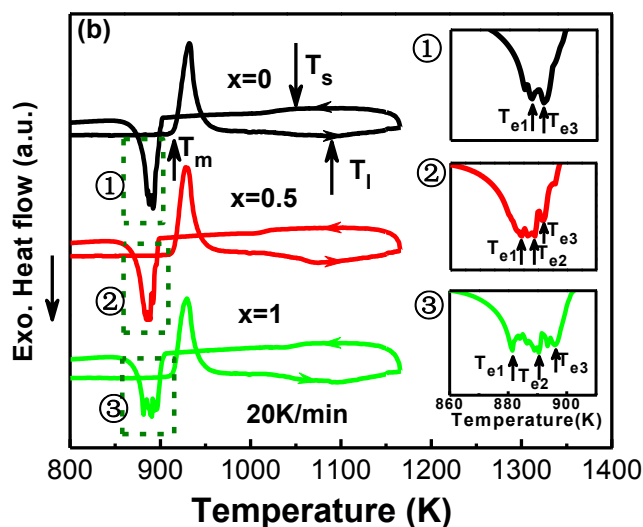


Figure 2. DSC curves of the as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) samples at spinning speed R_c of 25.6 m/s in (a) low and (b) high temperature ranges. The insets denote the magnified parts of the curves from 860 K to 900 K.

The onset crystallization temperature (T_x), the onset and end temperatures of the melting process (T_m and T_l), the onset temperature of solidification process (T_s), and the eutectic temperatures for three sub peaks (T_{e1} , T_{e2} and T_{e3}), supercooling degree ΔT and glass formability indices (T_{rx} and α), which are calculated from the DSC curves, are listed in Table 1. The ΔT ($= T_l - T_s$) of alloys increases at first, then decreases with the increase of Au content, the values of these parameters T_x , T_{rx} ($= T_x/T_m$ [19]) and α ($= T_x/T_l$ [20]) decreases at first, then increases with a minimum at $x = 0.5$, suggesting a nonmonotonic change of GFA with the addition of Au. Here, the liquidus temperatures T_l of three alloys are much higher than the melting point of pure Al (933 K), and thus the primary solidification should be hypereutectic type, i.e. the primary solidified phase is intermetallic phase rather than pure Al. Meanwhile, the sub peaks for eutectic exothermic process are in range from 880 K to 895 K. It is known that in binary Al-Y, Al-Au and Al-Fe phase diagrams the eutectic temperatures in Al-rich sides are 918, 923 and 928 K which can be reflected by the measured T_{e1} , T_{e2} and T_{e3} , respectively. Here the relative height of T_{e3} peak decreases with increasing x , suggesting that the amount of Fe atoms joining the primary solidification process increases. Thus, it is expected that the Al_5Fe_2 peak intensity in XRD increases and peak intensity for Al_3Y decreases at the same time (Fig. 1b).

Table 1. Thermal parameters of the as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy ribbons from the DSC curve at spinning speed R_c of 25.6 m/s

Comp.	T_x (K)	T_m (K)	T_l (K)	T_s (K)	T_{e1} (K)	T_{e2} (K)	T_{e3} (K)	ΔT (K)	T_{rx}	α
$x = 0$	508.4	915.9	1089.1	1049.7	887	-	892	39.4	0.56	0.47
$x = 0.5$	496.1	915.5	1074.8	1027.9	884	887	892	46.9	0.54	0.46
$x = 1$	506.5	915.0	1089.9	1061.6	881	889	895	28.3	0.55	0.46

3.1.3 Corrosion behavior of as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy alloys and their master alloys

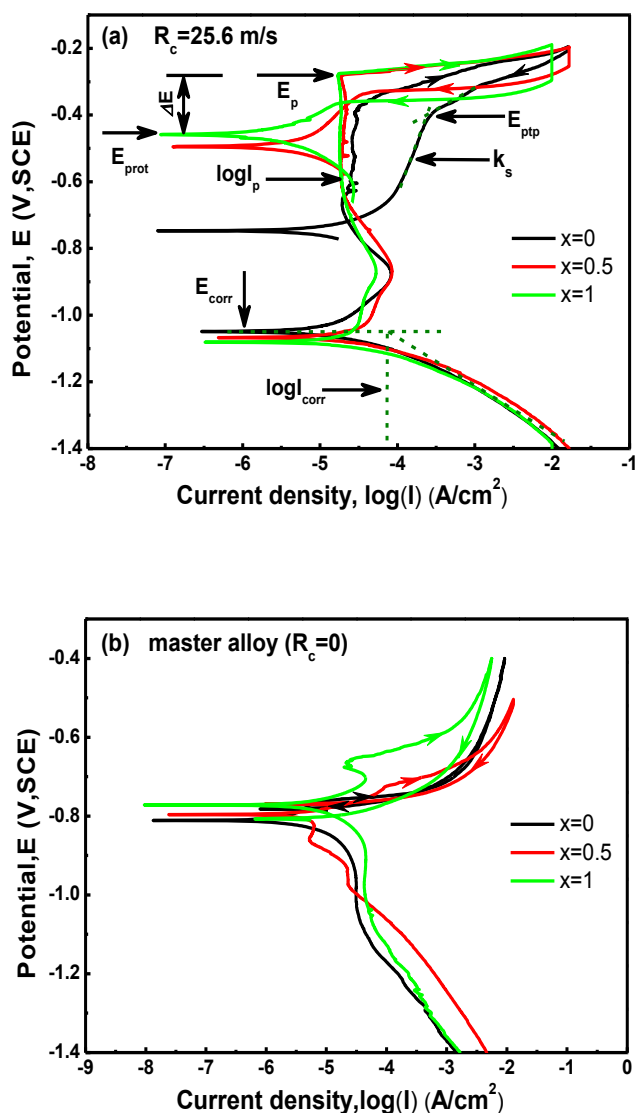


Figure 3. Potentiodynamic polarization curves of (a) as spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) samples at spinning speeds R_c of 25.6 m/s and (b) master alloys ($R_c = 0$) in 3.5 wt% NaCl solution.

Fig. 3 shows the single potentiodynamic cyclic polarization curves of the as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy alloys and their master alloys in 3.5 wt.% NaCl solution. The polarization parameters such as the corrosion potential E_{corr} , the logarithm of passivation current density $\log(I_p)$, pitting potential E_p , pit transition potential E_{ptp} , protection potential E_{prot} , potential difference ΔE ($= E_p - E_{\text{prot}}$) and steepness k_s ($= dE/d\log(I)$) on reverse scan are labeled in Fig. 3a. In reverse scanning process, E_{ptp} is the pit transition potential, E_{prot} is the protective potential, i.e. the potential at which the current density reaches the lowest anodic current value, and k_s is the slope of potential decreased with current below E_{ptp} . With adding Au element, the E_p of samples is obviously

improved and their passive region becomes wider. At the same time, their ΔE decreases significantly. These results indicate that the addition of Au plays an important role to the spontaneous passivation and repassivation behavior upon cyclic anodic polarization. Even more important, for the alloy with $x = 0$, there is an obvious transition with a large steepness (k_s) on the reverse scan of the Tafel curve (Fig. 3a), whereas with the addition of Au, the k_s of alloys decreases and their pitting transition becomes not evident. The corrosion potential (E_{corr}) of the master alloys increases with x . Although the master alloys don't show an evident passivation behavior, the addition of Au widens the passive region to some extent (Fig. 3b).

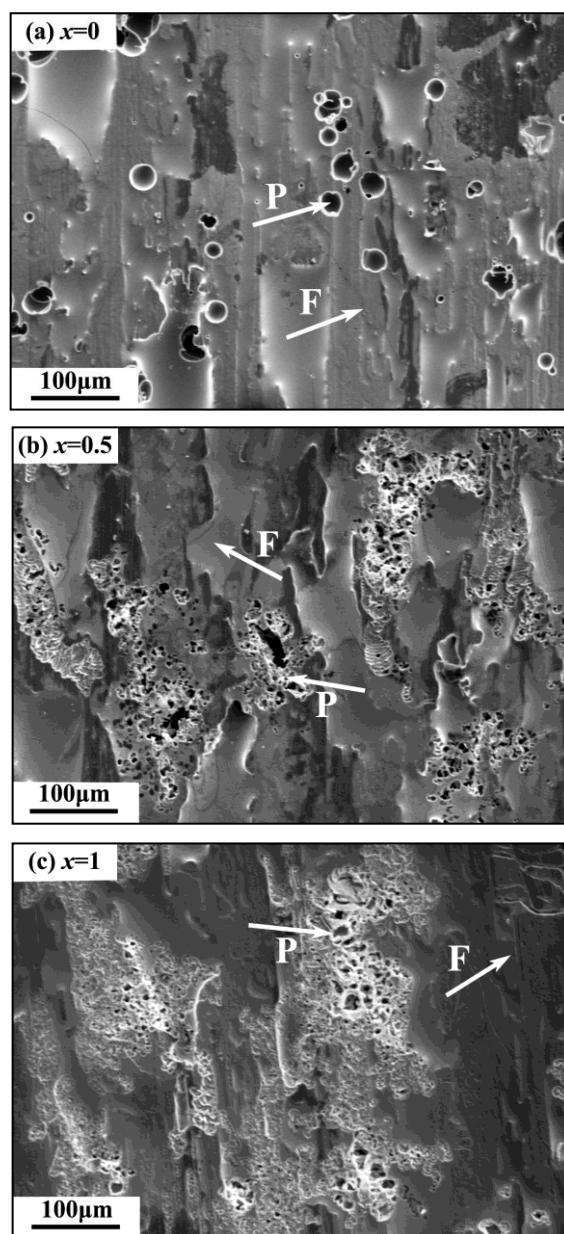
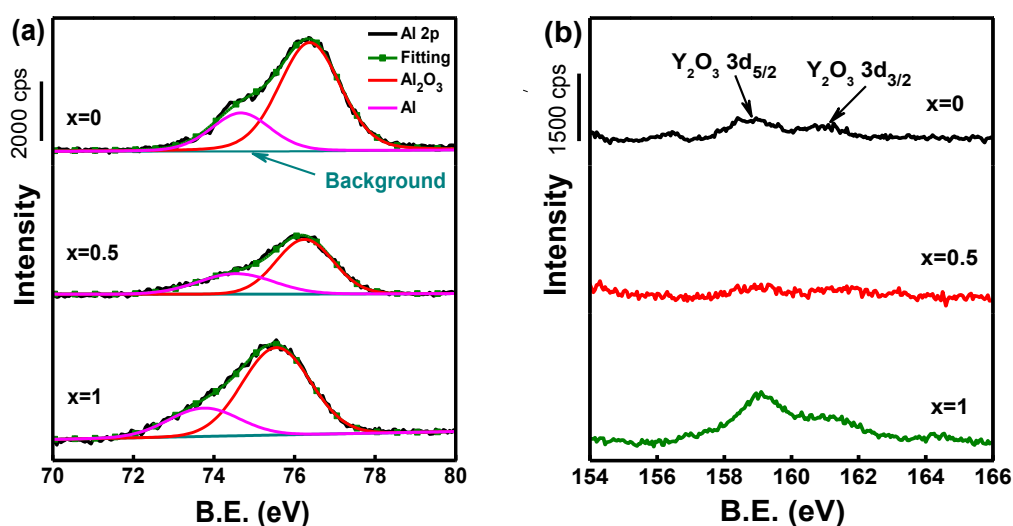


Figure 4. SEM micrographs of free surfaces of the $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy ribbons in 3.5 wt% NaCl solution: (a) $x = 0$, (b) $x = 0.5$ and (c) $x = 1$. The film matrix is labeled as F and the pitting region is labeled as P for the EDS region.

To better understand the effect of the Au addition on the pitting corrosion behavior of the present alloys, the surface morphologies of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) ribbons after electrochemical corrosion were observed by SEM and shown in Fig. 4. The pits of the amorphous ribbons with $x = 0$ are larger than that of ribbons with $x = 0.5$ and 1 . Moreover, after adding Au element the pits decrease their size significantly and agglomerate together in local regions (Fig. 4b and c). The element contents by EDS analysis on the pitting region and film matrix of the measured ribbons are listed in Table 2. Here, the pitting region is denoted with P and the film matrix region is denoted with F. The contents of Al and Y in the pits are lower than the corresponding component of the alloys, indicating the Al and Y dissolve into the solution preferentially [21]. The ratio of $c_{\text{Fe}}/c_{\text{Al}}$ of the corrosive matrix increases with the addition of Au while the $c_{\text{Y}}/c_{\text{Al}}$ decreases. Moreover, the oxygen content sharply increases with adding Au element, suggesting that an oxide film is formed in the surface of the samples.

Table 2. Atomic fraction of elements on the surface of the $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy ribbons by EDS after electrochemistry corrosion

Comp.	Position	c_{Al} (at%)	c_{Fe} (at%)	$c_{\text{Fe}}/c_{\text{Al}}$	c_{Y} (at%)	$c_{\text{Y}}/c_{\text{Al}}$	c_{Au} (at%)	c_{O} (at%)
$x = 0$	P	63.44	27.42	0.43	2.48	0.039	0	6.67
	F	84.28	4.72	0.056	6.57	0.078	0	4.43
$x = 0.5$	P	65.51	5.25	0.080	4.54	0.069	4.99	19.71
	F	80.35	4.84	0.060	5.90	0.073	0	8.91
$x = 1$	P	34.28	4.72	0.14	3.96	0.12	21.52	35.53
	F	51.68	3.53	0.068	3.57	0.069	1.02	40.19



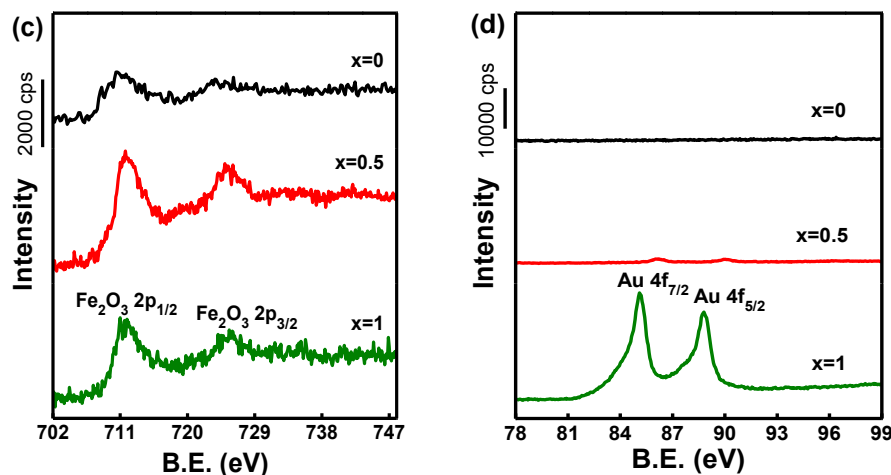


Figure 5. The fitted XPS spectra of as-spun corroded $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy ribbons: (a) Al 2p, (b) Y 3d, (c) Fe 2p and (d) Au 4f.

In order to provide more information about the passive film formed during the electrochemical test, the X-ray photoelectron spectroscopy (XPS) technique was employed on the as-spun $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) glassy ribbons after the polarization test. Fig. 5 shows XPS spectra of Al 2p, Y 3d, Fe 2p and Au 4f recorded from the sample surfaces. The Al 2p spectrum is composed of two peaks (Fig. 5a). The lower binding energy peak at 72.8–75 eV is assigned to Al and the higher binding energy peak at 74.5–77 eV is the alumina (Al_2O_3). The total area of Al 2p of the ribbon with $x = 0$ is much larger than that with $x = 0.5$ and 1 , which is consistent with the analysis of EDS (Table 2). Moreover, it is interesting to find that when $c_{\text{Au}} = 0.5$ at.%, the total area of Al 2p is the smallest and it increases with x increasing from 0.5 to 1. The results of XPS are consistent with the analysis of EDS (Table 2). The spectrum Y 3d for Y_2O_3 has two peaks which are assigned to Y 3d_{5/2} and Y 3d_{3/2}, respectively (Fig. 5b). The peak intensity of the ribbon with $x = 0.5$ is lower than that with $x = 0$ and 1 , similar to the situation of Al 2p. The spectrum Fe 2p shows peaks at 709–713 eV and 722–730 eV (Fig. 5c), which are assigned to Fe_2O_3 2p_{1/2} and Fe_2O_3 2p_{3/2}. The peak intensity of the ribbons with $x = 0.5$ and 1 is much larger than that with $x = 0$, corresponding to EDS results (Table 2) and indicating that the addition of Au can facilitate the formation of a thicker ferric oxide passive film. Contrary to the spectrums of Al 2p and Y 3d, it is clear that the peak intensity of Fe 2p of sample $x = 0.5$ is up to the maximum. The spectrum Au 4f also exists two peaks which are respectively assigned to Au 4f_{7/2} and Au 4f_{5/2} and their intensity increases with Au content and is consistent with EDS results (Table 2 and Fig. 5d).

3.2 Low rate spun and annealed $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ ribbons

3.2.1 XRD patterns and TEM images of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ alloys

Fig. 6a shows the XRD pattern of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-spun ribbons with a cooling rate of 18.3 m/s, which is lower than that in Fig. 1a. Some crystallized phases of α -Al, Al_5Fe_2 and Al_2Au have

precipitated out and are embedded on the amorphous matrix. The types of intermetallic phases are consistent with the master alloy (Fig. 1b). Fig. 6b shows the XRD pattern of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ amorphous ribbons with R_c of 25.6 m/s annealed for 5 min at 573K. After annealing, the sharp crystalline peaks of α -Al appear on the XRD pattern, indicating the α -Al phase precipitates from the $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ amorphous matrix. The primary crystallized phase is different from that in primary solidification indicated by Fig. 2b. The precipitated phases of the annealed $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ ribbons are further clarified by TEM observation and selected area electron diffraction (SAED). Fig. 6c gives the bright field images, showing nanograins with the size of 50 ± 10 nm dispersed in the amorphous matrix. The SAED pattern further confirms the formation of the α -Al and Al_5Fe_2 phases (bottom left of Fig. 6c). Fig. 6d presents the corresponding HRTEM image. The atomic spacing in one direction is 2.34 Å, which is close to that (2.32 Å) of the (111) crystal plane of α -Al. In short, the precipitated phases in low rate spun and annealed ribbons are agreeing with the precipitates in the master alloy.

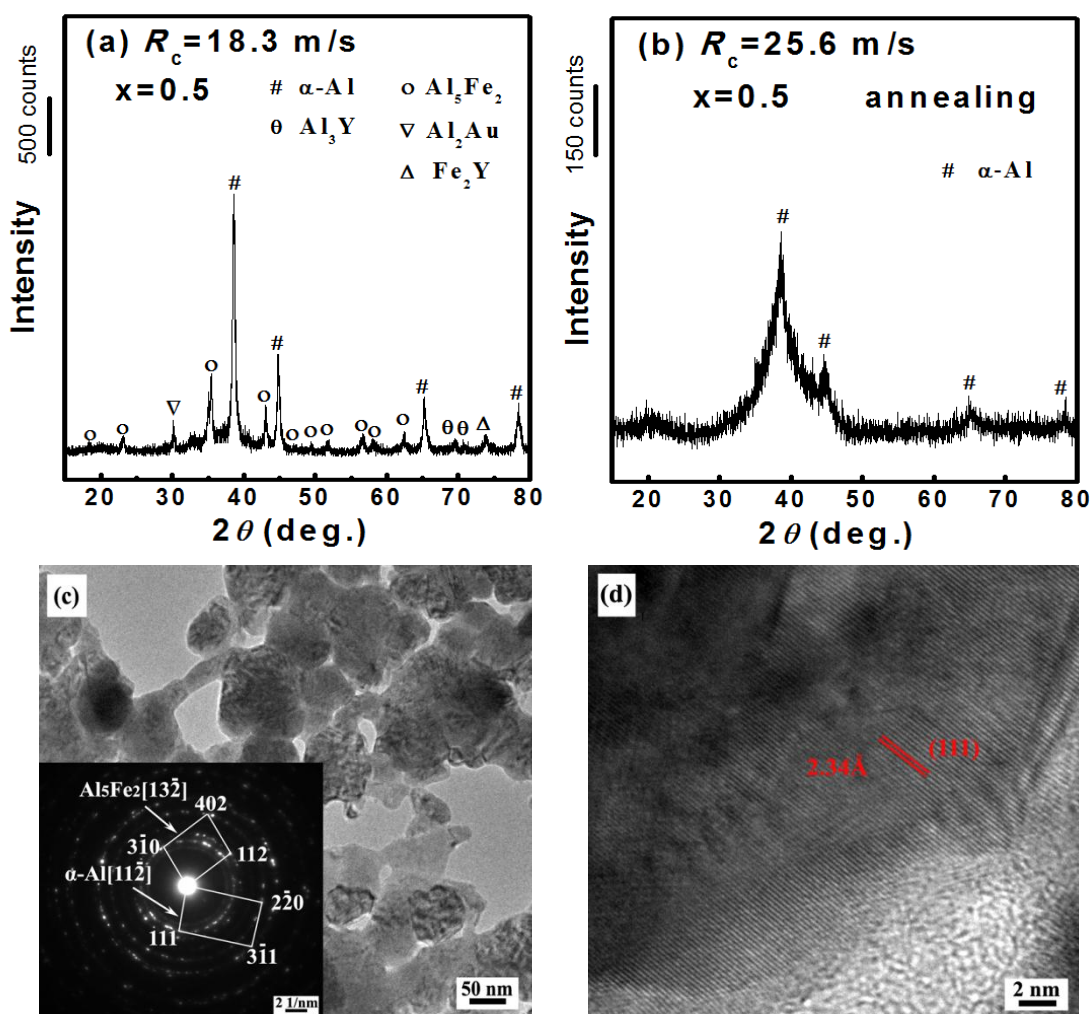


Figure 6. (a) XRD pattern of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-spun ribbons with a cooling rate of 18.3 m/s; (b) XRD pattern of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-spun ribbons with a cooling rate of 25.6 m/s annealed for 5min at 573K; (c) Bright field TEM image and the corresponding selected area electron diffraction (SAED) pattern of the annealing $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ ribbons; (d) HRTEM image in the selected zone in (c).

3.2.2 The corrosion behaviors of $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ alloy ribbons

Fig. 7 gives the single potentiodynamic cyclic polarization curves of the as-spun $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ alloy ribbons with R_c of 18.3 m/s and the annealed $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ alloy ribbons with R_c of 25.6 m/s. The low rate spun ribbon shows no obvious active/passive transition and has a poor pitting corrosion resistance. The annealed alloy exhibits an excellent passivation behavior with a wide passive region and the pit transition on reverse scan still retains. The polarization parameters of as spun ribbons, master alloys and annealed ribbons are all summarized in Table 3.

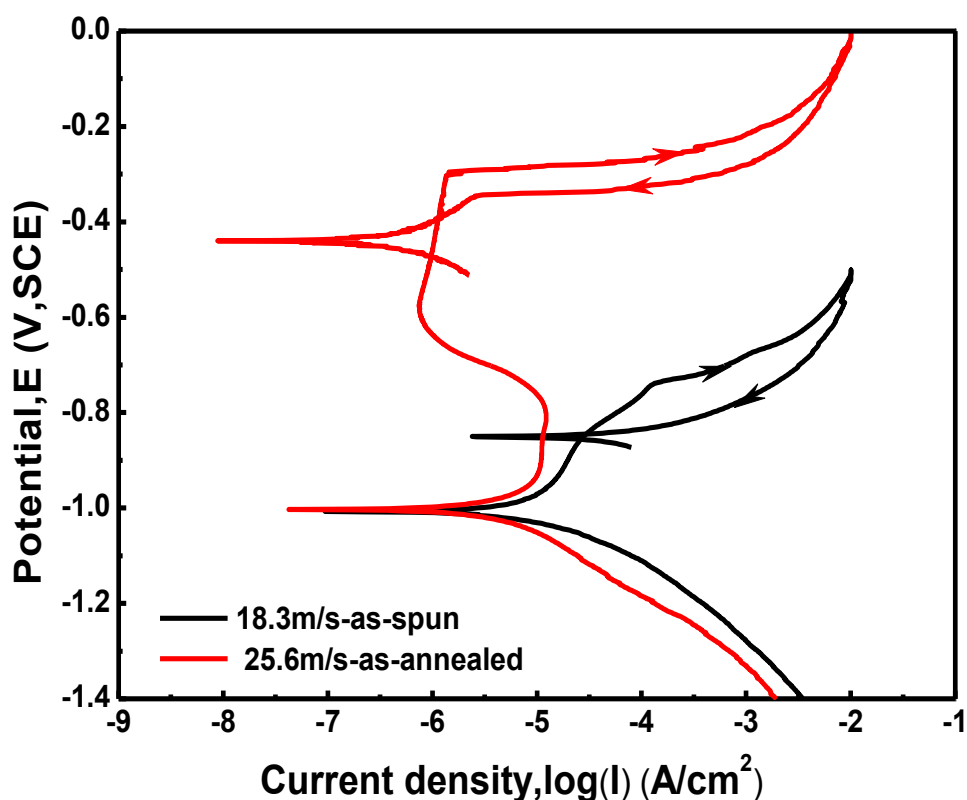


Figure 7. Potentiodynamic polarization curves of the $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-spun alloy ribbons with a cooling rate of 18.3 m/s and $\text{Al}_{87.5}\text{Fe}_5\text{Y}_7\text{Au}_{0.5}$ as-annealed ribbons with a cooling rate of 25.6 m/s in 3.5 wt% NaCl solution

The measured E_{prot} can be divided into two groups: -0.80 and -0.45 V_{SCE} . The first group includes master alloys, the low rate spun ribbon with $x = 0.5$ and the ribbon of with $x = 0$ and $R_c = 25.6$ m/s. The ribbons with $x = 0.5$ and 1 and $R_c = 25.6$ m/s as well as the annealed $x = 0.5$ ribbons belong to the second group. In addition, the E_{corr} of samples can also be divided into two groups: -1.00 and -0.80 V_{SCE} . Master alloys belong to the second group and the other samples belong to the first group, which indicates that E_{corr} are mainly dependant on the amorphous phase in the samples. Moreover, we can clearly see that after the annealing process the ΔE and k_s of the ribbon decrease, indicating that the precipitation of nanocrystalline phases $\alpha\text{-Al}$ and Al_5Fe_2 is helpful to repair the passivation films.

Table 3. The polarization parameters of potentiodynamic polarization curves of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloy ribbons with different R_c under as spun (a.s.), as cast (a.c.) and annealed conditions.

Condition	Alloys	E_{corr} (V)	E_{pit} (V)	I_{pit} (A/cm ²)	I_p (A/cm ²)	E_{ptp} (V)	E_{prot} (V)	ΔE (V)	k_s (V/dec)
$R_c = 25.6\text{m/s}$ (a.s.)	$x = 0$	-1.05	-0.39	2.82×10^{-5}	2.57×10^{-5}	-0.40	-0.75	0.36	0.56
	$x = 0.5$	-1.07	-0.28	1.86×10^{-5}	2.00×10^{-5}	-0.36	-0.49	0.21	0.23
	$x = 1$	-1.08	-0.28	1.70×10^{-5}	1.82×10^{-5}	-0.33	-0.46	0.18	0.11
$R_c = 0\text{m/s}$ (a.c.)	$x = 0$	-0.81	-0.76	6.61×10^{-6}	-	-	-0.78	0.02	-
	$x = 0.5$	-0.80	-0.73	9.12×10^{-5}	-	-	-0.77	0.04	-
	$x = 1$	-0.77	-0.66	2.24×10^{-5}	-	-	-0.81	0.15	-
$R_c = 18.3\text{m/s}$ (a.s.)	$x = 0.5$	-1.00	-0.74	1.23×10^{-4}	-	-	-0.85	0.11	-
$R_c = 25.6\text{m/s}$ (annealed)	$x = 0.5$	-0.99	-0.30	1.45×10^{-6}	1.02×10^{-6}	-0.34	-0.44	0.14	0.13

4. DISCUSSION

4.1 The intermetallic precipitation tendency and glass forming ability of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys

The atomic packing efficiency can be thought about to deduce the precipitation type and compare the glass forming ability (GFA) of different alloys [22, 23]. According to Miracle's efficient cluster packing (ECP) model [24, 25], we can know the relationship of the atomic radius ratio (R) of the solute to solvent elements and the theoretical coordination number (N^T):

$$N^T = \begin{cases} 4\pi / \left\{ 6 \arccos \left[\sin \left(\frac{\pi}{3} \right) \sqrt{1 - \frac{1}{(R+1)^2}} \right] - \pi \right\} & \text{for } 0.225 \leq R < 0.414 \\ 4\pi / \left\{ 8 \arccos \left[\sin \left(\frac{\pi}{4} \right) \sqrt{1 - \frac{1}{(R+1)^2}} \right] - 2\pi \right\} & \text{for } 0.414 \leq R < 0.902 \\ 4\pi / \left\{ 10 \arccos \left[\sin \left(\frac{\pi}{5} \right) \sqrt{1 - \frac{1}{(R+1)^2}} \right] - 3\pi \right\} & \text{for } R \geq 0.902 \end{cases} \quad (1)$$

The theoretical coordination number (N^T) reflects the most efficient or optimum structure of a tightly packed cluster [25]. In present alloys, it is thought that the solute atoms Fe, Y and Au atoms are surrounded only by the Al solvent atoms, such that the N^T -values of Fe, Y and Au are calculated to be 11.13, 16.52 and 13.53, respectively.

From a topological point of view, the practical coordination number (N) of a central atom should be an integer in the neighborhood of the N^T . Thus, we can assume that the N -values of Fe-centered clusters are mainly 10, 11 and 12, Y-centered clusters are 15, 16 and 17 and Au-centered clusters are 12, 13 and 14. The corresponding atomic packing efficiency can be calculated by the following equation:

$$\varepsilon = \begin{cases} N / N^T & N \leq N^T \\ \left(r_{\text{solute}} / (R_N^* \times r_{\text{Al}}) \right)^3 & N > N^T \end{cases} \quad (2)$$

where R_N^* obtained from equation (1), is the specific value of radius ratio corresponding to N , r_{solute} is the atomic radii of solute atoms Fe, Y and Au, r_{Al} is the atomic radius of Al atoms [25]. We use the effective atomic radii instead of the nominal radii to calculate the packing efficiency. The packing efficiency (ε_{AIM}) and the average atomic packing efficiency ($\bar{\varepsilon}_{\text{M}}$) of different solute (M)-centered clusters are listed in Table 4.

Table 4. Theoretical coordination number N_T and packing efficiencies (ε_{AIM}) and the average atomic packing efficiency ($\bar{\varepsilon}_{\text{M}}$) of different solute (M)-centered clusters.

Centered element(M)	r(nm)	N^T	Cluster	ε_{AIM} (%)	$\bar{\varepsilon}_{\text{M}}$ (%)
Fe	0.128	11.13	Al ₁₀ Fe	89.85	95.47
			Al ₁₁ Fe	98.83	
			Al ₁₂ Fe	97.72	
Y	0.174	16.52	Al ₁₅ Y	90.80	93.44
			Al ₁₆ Y	96.85	
			Al ₁₇ Y	92.68	
Au	0.145	13.53	Al ₁₂ Au	88.69	91.87
			Al ₁₃ Au	96.08	
			Al ₁₄ Au	90.84	

We can see that $\bar{\varepsilon}_{\text{Au}}$ is obviously lower than $\bar{\varepsilon}_{\text{Fe}}$ and $\bar{\varepsilon}_{\text{Y}}$ so that the total atomic packing efficiency (ε) of Al-Fe-Y alloys is declined by substituting Au for Fe and Y. From a topological standpoint, the low packing efficiency reflects the weak atomic interactions between the constitute atoms and the atomic rearrangement towards a crystallized state during solidification will be easier [26]. As $x = 0$, the $\bar{\varepsilon}_{\text{Fe}}$ is higher than $\bar{\varepsilon}_{\text{Y}}$. And during the solidification, the AlY cluster will precipitate out easily. As $x = 0.5$ and 1, the $\bar{\varepsilon}_{\text{Au}}$ is closer to $\bar{\varepsilon}_{\text{Y}}$ and much lower than $\bar{\varepsilon}_{\text{Fe}}$. As pointed out by Yang [27], the densest part of amorphous matter can also be the start point to trigger the

destabilization. Hence, the AlFe cluster will precipitate out from the melt. So the precipitated intermetallic phases in Fig. 1b can be easily understood. Generally, the addition of Au can decrease the ε of the alloy, and it is understood that the GFA is decreased by Au addition. However, the alloys have a monotonic change of GFA with x , i.e. the GFA of $x = 0.5$ is minimum (Fig. 2a). There should be other factor influencing the GFA of present alloys.

Based on three empirical rules of obtaining the high GFA alloy, the GFA of alloys can be scaled by the thermodynamic composite parameter F explanations by Takeuchi and Inoue [28, 29], i.e. the absolute product of the mixing enthalpy (ΔH^{chem}) and mismatch entropy normalized by the Boltzmann constant (S_{σ}/k_B), which is calculated as shown in Appendix. Table 5 shows the values of the mixing enthalpy (ΔH^{chem}), the mismatch entropy normalized by the Boltzmann constant (S_{σ}/k_B) and the thermodynamic composite parameter F ($|\Delta H^{\text{chem}} \times S_{\sigma}/k_B|$). With the addition of Au, ΔH^{chem} becomes more negative and $|\Delta H^{\text{chem}} \times S_{\sigma}/k_B|$ becomes larger. Therefore, the GFA of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys will be expected to be in the order of $x = 0 < x = 0.5 < x = 1$. Considering both atomic packing efficiency and thermodynamic driving force for the glass formation, it is expected that the GFA of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys decreases at first, then increases with the addition of Au.

Table 5. The mixing enthalpy (ΔH^{chem}), the mismatch entropy normalized by the Boltzmann constant (S_{σ}/k_B) and the thermodynamic composite parameter F ($|\Delta H^{\text{chem}} \times S_{\sigma}/k_B|$).

Alloys	ΔH^{chem} (kJ/mol)	S_{σ}/k_B	F
$x=0$	-11.31	0.07969	0.90
$x=0.5$	-11.73	0.07930	0.93
$x=1$	-12.14	0.07886	0.96

4.2 The pit transition and repassivation of $\text{Al}_{88-x}\text{Fe}_5\text{Y}_7\text{Au}_x$ ($x = 0, 0.5$ and 1) alloys

In general, the corrosion resistance of the alloys can be greatly influenced by the chemical composition [30-34]. Gold is a noble element and it is expected that ΔE of the alloys decreases with increasing gold content x (Table 3). For master alloys, the protection potential E_{prot} is close to their corrosion potential E_{corr} without obvious passivation. It indicates that the amorphous phase makes a great contribution for the passivation. Moreover, in case of $R_c = 25.6$ m/s, the E_{prot} of the alloy with $x = 0$ is about -0.8 V_{SCE}, while the E_{prot} of alloys with $x = 0.5$ and 1 is -0.4 V_{SCE}. It is possible that the Y-rich intermetallic shift the protection potential negatively, according to the corrosion potential by intermetallic phases in earlier work [35].

Newman et al. [36] found that some tunnels existed in the pit interiors and suggested that the pits transition phenomenon in the reverse scan is caused by the transition to tunnelling. Comotti et al. [37] found that the steepness of the pitting transition below the pit transition potential E_{ptp} was related to the shape of pits. The large and deep cavities have a geometrical constriction effect, thus the pits

repassivation becomes more difficult and the obvious pitting transition phenomenon arises on the reverse scan, while the small and shallow pits can repassivate readily and the transition becomes less apparent. Hence, it is understood that the steepness k_s and pits size of the alloys decrease with the increasing x (Table 3 and Fig. 4).

It is clear that the Au addition can aggravate the precipitation of AlFe phases during the solidification and AlFe intermetallic has a higher corrosion potential than that of AlY intermetallic. It is understood that the concentration of Fe in the polarized matrix increases with the addition of Au and the c_{Fe} in the pits is higher than that in the film (Table 2). In addition, it is because of the enrichment of the noble metal Au element which has the excellent corrosion resistance and can inhibit the forming of tunnels, a layer of more stable passive film which is mainly composed of the ferric oxide and Au forms on the corrosion surface. Accordingly, the ribbons with Au addition exhibit an excellent spontaneous passivation and repassivation behavior upon cyclic anodic polarization curves (Fig. 3).

The annealed $Al_{87.5}Fe_5Y_7Au_{0.5}$ nanocrystalline alloys also show an obvious passivation behavior on the forward scan and the pitting transition phenomenon on the repassivation process (Fig. 7), suggesting that the precipitates like α -Al and Al_5Fe_2 formed in annealing treatment have no harmful effect on the passivation and pitting transition of alloy ribbons. Moreover, the k_s of the annealed sample is lower than that of the as spun samples (Fig. 7 and Table 3), indicating that the nanocrystallines have a beneficial effect on the repassivation. In short, the large AlFe intermetallic precipitation tendency and high amorphous phase fraction in Al-Fe-Y glassy alloy are helpful for improving its repair passive film ability and hauling the pits transition, which gives a clue to increase the corrosion resistance of Al-based glassy alloys.

5. CONCLUSIONS

The effects of Au addition on selective intermetallics precipitation and corrosion behaviors of the as-spun $Al_{88-x}Fe_5Y_7Au_x$ ($x = 0, 0.5$ and 1) alloys have been investigated. We find:

(1) The precipitation of AlY or AlFe phases is related to the atomic packing efficiency which changes with the increasing Au content x . In case of $x = 0$, due to the atomic packing efficiency of AlY cluster is lower than AlFe cluster, the AlY phase preferentially precipitate out; whereas in case of $x = 0.5$ and 1 , the higher packing efficiency of the AlFe cluster can be the start point to trigger the destabilization so that the AlFe phase precipitates more easily.

(2) The different type clusters make great effects on the passivation and pitting transition of $Al_{88-x}Fe_5Y_7Au_x$ ($x = 0, 0.5$ and 1) alloys with $R_c = 25.6$ m/s. When $x = 0$, the ΔE ($= E_p - E_{prot}$, E_p and E_{prot} are piting and protective potentials) and steepness k_s ($= dE/d\log(I)$) on reverse scan of the alloy which has more AlY clusters are larger, suggesting that the pit interiors have formed some tunnels and the repassivation becomes more difficult; meanwhile, after adding 0.5 and 1 at% Au, the ΔE and k_s of the alloys which precipitate more Al_5Fe_2 are lower obviously.

(3) The large AlFe intermetallic precipitation tendency and high fraction of amorphous phase benefit for repairing the passive film and inhibiting the pits transition. In case of $x = 0.5$, comparing the annealed alloy with $R_c = 25.6$ m/s and as spun alloy with $R_c = 18.3$ m/s, a small amount

of α -Al and Al_5Fe_2 precipitates have no harmful effect on the repassivation and pitting transition of alloy ribbons, while a large amount of intermetallic precipitates are different.

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APPENDIX

According to the regular solution model [28, 38]:

$$\Delta H^{\text{chem}} = \sum_{\substack{i=1 \\ i \neq j}} \Omega_{ij} c_i c_j \quad (1)$$

where c_i and c_j are the concentrations of i and j elements in the multi-component alloy, respectively. Ω_{ij} is regular solution interaction parameter between i -th and j -th elements. Ω_{ij} can be expressed as:

$$\Omega_{ij} = 4 \times \Delta H_{AB}^{\text{mix}} \quad (2)$$

$\Delta H_{AB}^{\text{mix}}$ is the mixing enthalpy of binary liquid alloys.

The mismatch entropy normalized by Boltzmann constant (S_σ/k_B) are calculated by Eq. (3):

$$S_\sigma/k_B = \frac{3}{2}(\zeta^2 - 1)y_1 + \frac{3}{2}(\zeta - 1)^2 y_2 - \left[\frac{1}{2}(\zeta - 1)(\zeta - 3) + \ln \zeta \right] (1 - y_3) \quad (3)$$

where ζ is defined as $\zeta = 1/(1 - \eta)$ with the packing fraction η taken the value of 0.64. y_1 , y_2 and y_3 have a relation of $y_1 + y_2 + y_3 = 1$ and defined as Eqs. (4) - (6):

$$y_1 = \frac{1}{\sigma^3} \sum_{j>i=1} (d_i + d_j)(d_i - d_j)^2 c_i c_j, \quad (4)$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2} \sum_{j>i=1} d_i d_j (d_i - d_j)^2 c_i c_j, \quad (5)$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2}, \quad \sigma^k = \sum_{i=1} c_i d_i^k, \quad k = 2, 3, \quad (6)$$

Here d_i^k is the atomic diameter of i-th element. The large S_σ/k_B and ΔH^{chem} are deemed to be beneficial to stabilize the amorphous structure.

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