Effects of W Addition on the Electrochemical Behaviour and Passive Film Properties of Fe-Based Amorphous Alloys in Acetic Acid Solution

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Abstract

The electrochemical behaviour and passive film properties of Fe–Cr–Mo–W–C–B–Y amorphous alloys in acetic acid solution were investigated. The potentiodynamic polarisation and Nyquist curves demonstrated that W addition significantly enhanced the corrosion resistance. Mott–Schottky plots and angle-resolved X-ray photoelectron spectra indicated that passive films with different W contents exhibited dipolar (p – n) semiconducting characteristics separated by flat-band potentials. The outer and inner oxide layers of the passive films were modified by reducing the acceptor and donor densities. Moreover, W addition favoured the formation of a thicker and more stable passive film to inhibit the dissolution of alloy elements.

Keywords Amorphous alloy · XPS · Mott–Schottky measurement · Passive film · Semiconducting property · Chemical ingredient

1 Introduction

Acetic acid (CH_3COOH) is one of the most widely used organic reactants in chemical and petrochemical industries [1, 2]. Reaction vessels and storage tanks containing acetic acid are typically made of stainless steel, which exhibits excellent corrosion resistance within certain temperature and concentration ranges [2]. However, the stainless steel vessels often undergo severe corrosion in the presence of inorganic acids and salts [3]. As a new emerging material,

Fe-based bulk metallic glasses (BMGs) possess more excellent corrosion resistance compared with crystalline steels due to the absence of defects, including grain boundary, dislocation, component segregation and inclusion [4], and therefore they are one of the potential engineering materials used in acetic acid-corrosive environments.

In the past decades, a series of nonferromagnetic Fe–Cr–Mo–C–B–Y/Ln BMGs with high glass-forming ability (GFA) and excellent corrosion resistance have been developed [5–8]. Numerous studies have investigated the corrosion behaviour and passive film properties of Fe-based BMGs in inorganic solutions, such as inorganic acids (e.g. hydrochloric acid [9–11] and sulphuric acid [4, 11, 12]), inorganic salts (e.g. sodium chloride [4, 13, 14], sodium sulphate [15], and calcium chloride [16]), and alkaline solutions (e.g. sodium hydrate [4]). However, the corrosion behaviour of Fe-based BMGs in the organic acid solutions, particularly acetic acid, has not yet been comprehensively clarified. Generally, the corrosion mechanism of alloys in acetic acid is more complex than that in inorganic acid solutions [2, 17]. As a weak acid, acetic acid can activate a large number of initial pitting sites through dissociation process of aggressive species (e.g. H^+ and CH_3COO^-) [18], whereas the

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reduction of the undissociated acetic acid plays a dominant role as a reactant and thus enhances the cathodic reactions [1, 19]. Acetic species in acetic acid solution could also act as a weak inhibitor of the anodic dissolution of stainless steel by affecting the protectiveness of passive layers [20]. A previous study of the electrochemical behaviour of 316L stainless steel in acetic acid solution indicated the importance of local enrichment of Mo in initiating passivation [3].

Adding minor refractory elements (e.g. Mo and W) into Fe-based BMGs is an effective approach to improve the corrosion resistance in inorganic solutions by preventing the dissolution of alloy elements [21] or increasing the stability and uniformity of passive films [13]. Adding W element to Fe-based BMGs is beneficial for corrosion resistance because it prevents the dissolution of alloy elements even in concentrated hydrochloric acid solutions [22–24]. Furthermore, W addition is more effective than Mo addition to improve the corrosion resistance due to its high stability at low potentials [24]. In particular, the dissolution potential of W^{6+} oxide is higher than that of Mo^{6+} oxide, and all W oxides are considered insoluble in both inorganic and organic acid solutions [25, 26].

In this study, the electrochemical behaviour of Fe–Cr–Mo–W–C–B–Y amorphous alloys in acetic acid solution was investigated in detail. Angle-resolved X-ray photoelectron spectroscopy (XPS) and Mott–Schottky analyses were conducted to determine the semiconducting property, chemical ingredient, and valence electron state of the passive films formed in acetic acid solutions. The effects of W addition on corrosion behaviour and passive film properties were discussed systematically.

2 Experimental

2.1 Specimen Preparation

Alloy ingots of Fe-based alloy with a nominal composition of $Fe_{47-x}Cr_{20}Mo_{10}W_xC_{15}B_6Y_2$ ($x = 0, 2, 4, 6$ at.%) were prepared by arc melting the mixture of pure Fe (99.7 wt%), Cr (99.98 wt%), Mo (99.9 wt%), C (99.999 wt%), W (99.5 wt%), Y (99.6 wt%) and pre-alloyed FeB (99.38 wt%) in a Ti-gettered argon atmosphere. Approximately 40- μ m-thick and 1–1.2-mm-wide glassy ribbons were produced by the single-roller melt-spinning method in an argon atmosphere with a wheel speed of 35 m/s.

The structure of Fe-based amorphous ribbons was examined by X-ray diffraction (XRD) with $Cu K_{\alpha}$ radiation. The thermal stability of the melt ribbons was determined using the NETZSCH 404 differential scanning calorimeter (DSC) with a heating rate of 20 K/min.

2.2 Electrochemical Measurements

Electrochemical measurements were taken on Gamry Reference 600 electrochemical work station. All electrochemical tests were performed in a three-electrode cell using a platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potential state in this study was based on the SCE. 1 mol/L acetic acid solution was used as electrolyte and prepared from analytical reagent-grade acetic acid and deionised water. Prior to the electrochemical experiments, the wheel side of the ribbon samples was mechanically ground with a 2000-grit metallographic sandpaper and cleaned with ethanol. The free side of the ribbon was sealed with a mixture of paraffin and colophony. The ribbon samples were initially polarised to -1.2 V for 3 min to remove the oxide film formed in air. The experiments were started until the open-circuit potential (OCP) became stable after immersion in the electrolyte for 30 min. Electrochemical impedance spectroscopy (EIS) measurement of the ribbon samples was performed at the OCP with a sinusoidal amplitude of 10 mV at a frequency range from 10^5 to 10^{-2} Hz. The measured EIS plots were interpreted and fitted on the basis of the equivalent circuit by using ZSimpWin software. The potentiodynamic polarisation shifted from -0.4 V to $+1.2$ V with a scan rate of 0.33 mV/s in the electrolyte.

Mott–Schottky tests of the passivated ribbons were conducted by performing a potential scan from 0.1 to 0.9 V with a scan rate of 20 mV/s to evaluate the semiconducting properties of the passive films. Prior to the Mott–Schottky tests, the melt ribbons were immersed in 1 mol/L acetic acid solution at the OCP for 120 h to obtain stable passive films [10, 27]. All electrochemical measurements were conducted at room temperature, and each test was repeated at least three times to ensure good repeatability.

2.3 Angle-Resolved XPS Measurement

The chemical distribution and thickness of passive films were analysed with the Axis Ultra XPS using a monochromated AlK_{α} X-ray source (X-ray photon characteristic energy, $h\nu = 1486.6$ eV). Pure Au sample was used to calibrate the binding energy by setting the $Au 4f_{7/2}$ peak at the binding energy of 83.96 ± 0.02 eV. Fermi edge was calibrated using pure Au and setting the binding energy at 0.00 ± 0.02 eV. The XPS spectra of different elements were analysed with CasaXPS software. The standard binding energies of Fe 2p, Cr 2p, Mo 3d, and W 4f core levels were determined according to the NIST XPS database. Prior to the XPS analysis, Fe-based amorphous ribbons were immersed in 1 mol/L acetic acid solution for

120 h at room temperature. After the immersion corrosion tests, the samples were ultrasonically cleaned three times to remove any surface contaminations.

The principle of the angle-resolved XPS analysis is shown in Fig. 1. The effective information depth (d_e) of the passive film varies with the emission angle (θ). The thickness (d) of the passive film can be calculated from the analysis of the XPS spectrum by using the oxide-to-metal peak intensity ratio ($I_{\text{ox}}/I_{\text{met}}$) according to Eq. (1) [28, 29]:

$$\frac{d}{\lambda} = \ln \left(1 + \frac{I_{\text{ox}}}{I_{\text{met}}} \frac{V_{\text{met}}}{V_{\text{ox}}} \right) / \sec \theta, \quad (1)$$

where $V_{\text{met}}/V_{\text{ox}}$ is the ratio of the atom volume densities in the metal and oxide states, and λ is the inelastic mean free paths for a metal atom. The value of d can be obtained by the regression analysis of d/λ at various emission angles. In this study, angle-resolved XPS analysis was performed at emission angles of 0°, 15°, 30° and 45°.

3 Results

3.1 Characterisation and Electrochemical Measurements of Fe-Based Amorphous Alloys

As shown in Fig. 2a, the XRD patterns of $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_xC_{15}\text{B}_6\text{Y}_2$ melt ribbons exhibit only broad hump peaks without any crystalline peaks. All DSC curves (Fig. 2b) show obvious glass transition characteristics from 854 to 881 K. The XRD and DSC results indicate a complete amorphous structure of Fe-based alloy ribbons.

The typical potentiodynamic polarisation curves of Fe-based amorphous alloys obtained in the electrolyte exposed to air at 298 K are depicted in Fig. 3a. The potentiodynamic polarisation curves of all Fe-based amorphous alloys have a similar profile, which shows a wide current density plateau associated with the passive film formation and a dramatic increase in current intensity, implying the dissolution of passive films. All of the samples spontaneously passivate with a current density in the order of $1 \mu\text{A}/\text{cm}^2$,

which indicates the excellent corrosion resistance of Fe-based amorphous alloys in 1 mol/L acetic acid solution. EIS measurements were executed to identify the electrochemical properties of Fe-based amorphous alloys in acetic acid solution. As shown in Fig. 3b, all Nyquist plots present only one capacitive loop, illustrating one single time constant in the electrochemical measurement [31]. Moreover, the semicircle diameter in the Nyquist plots increases with W addition. On the basis of the previous analysis, the equivalent circuit to simulate the EIS results of Fe-based amorphous ribbons is shown in the inset of Fig. 3b, where R_s , R_c , and Q are the solution resistance, charge transfer resistance, and possibility of a nonideal capacitance, respectively. The electrochemical parameters, including the corrosion potential (E_{corr}), corrosion current density (i_{corr}), passive current density (i_{pass}), and fitted R_c , are listed in Table 1. As increase the W content from 0 to 6 at.%, the values of i_{pass} decreases from 2.70 to $1.22 \mu\text{A}/\text{cm}^2$, whereas R_c significantly increases from approximately 188.55 to $960.15 \text{ k}\Omega \text{ cm}^2$. A high R_c indicates a stable passive film and superior corrosion resistance [32]. Therefore, the EIS fitted data are highly coincident with the potentiodynamic polarisation results, namely W addition can enhance the corrosion resistance of Fe-based amorphous alloys in 1 mol/L acetic acid solution.

3.2 Mott–Schottky Results of Fe-Based Amorphous Alloys

According to the electrochemical results, the novel Fe–Cr–Mo–W–C–B–Y amorphous ribbons exhibit excellent corrosion resistance in acetic acid solution. The electrochemical behaviour of the passive film is related to its semiconducting properties, which is evaluated by Mott–Schottky analysis using the measured electrode capacitance as a function of the electrode potential. The passive film–electrolyte interface capacitance C_f measured by the Mott–Schottky tests can be expressed in Eq. (2) [33]:

$$C_f^{-1} = C_{\text{SC}}^{-1} + C_{\text{H}}^{-1}, \quad (2)$$

where C_{SC} is the space charge capacitance, and C_{H} is the capacitance of Helmholtz layer. In general, the value of C_{H} for different metals or alloys is approximately $50 \mu\text{F cm}^{-2}$ [34]. C_f is frequency dependent [35, 36]:

$$C_f = (-Z_{\text{im}} \cdot 2\pi f)^{-1}, \quad (3)$$

where Z_{im} is the imaginary part of the interfacial impedance, and f is the test frequency. Figure 4 presents the correlations between C_f and f for $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_xC_{15}\text{B}_6\text{Y}_2$ ribbons, which were calculated from the EIS analysis after the specimens immersed in 1 mol/L acetic acid solution at the OCP for 120 h. In the study of Paola et al.,

Fig. 1 Scheme of angle-resolved XPS [30]

Fig. 2 **a** XRD patterns; **b** DSC curves of $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ ($x = 0, 2, 4, 6$ at.%) melt ribbons

Fig. 3 **a** Potentiodynamic polarisation; **b** Nyquist curves (inset: the equivalent circuit, $R_s R_c Q$) of $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ ($x = 0, 2, 4, 6$ at.%) amorphous alloys in 1 mol/L acetic acid solution

Table 1 Electrochemical parameters of $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ ($x = 0, 2, 4, 6$ at.%) amorphous alloys in 1 mol/L acetic acid solution

W addition (at.%)	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	i_{pass} ($\mu\text{A}/\text{cm}^2$)	R_c ($\text{k}\Omega \text{ cm}^2$)
$x = 0$	-0.13 ± 0.04	0.20 ± 0.06	2.70 ± 0.27	188.55 ± 11.10
$x = 2$	-0.07 ± 0.03	0.17 ± 0.04	1.97 ± 0.16	483.50 ± 14.57
$x = 4$	-0.04 ± 0.05	0.12 ± 0.03	1.60 ± 0.11	729.35 ± 36.42
$x = 6$	-0.01 ± 0.02	0.11 ± 0.02	1.22 ± 0.13	960.15 ± 30.90

Fig. 4 Correlation between capacitance and frequency of the passivated $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ ($x = 0, 2, 4, 6$ at.%) ribbon specimens after immersion in 1 mol/L acetic acid solution at the OCP for 120 h

the Mott–Schottky analysis of the passive films revealed strong dispersion with f and a linear relationship between C_f^{-1} and $\ln f$ when the capacitance is nearly constant [37, 38].

The validity of the Mott–Schottky analysis is based on the assumption that C_{SC} is much smaller than C_{H} , and the measured capacitance mainly reflects the capacitance of the space charge layer of the passive film [39]. Equation (2) can also be given in the Mott–Schottky form:

$$C_f^{-2} = C_{\text{SC}}^{-2} + C_{\text{H}}^{-2} + 2C_{\text{SC}}^{-1} \cdot C_{\text{H}}^{-1}. \quad (4)$$

In this study, the measurement frequency was set at 10^3 Hz, where C_f is almost constant and much smaller than C_{H} , as shown in Fig. 4. Thus, the contributions of C_{H}^{-2} and

$2C_{SC}^{-1} \cdot C_H^{-1}$ in Eq. (4) can be negligible. The measured capacitance is equal to the space charge capacitance, and those of *p*-type (C_{SCp}) and *n*-type (C_{SCn}) semiconductors are expressed in Eqs. (5) and (6), respectively [35]:

$$C_{SCp}^{-2} = -\frac{2}{\varepsilon_0 \varepsilon_r N_A e} \left(E - E_{FB} - \frac{kT}{e} \right), \quad (5)$$

$$C_{SCn}^{-2} = \frac{2}{\varepsilon_0 \varepsilon_r N_D e} \left(E - E_{FB} - \frac{kT}{e} \right), \quad (6)$$

where ε_r is the dielectric constant of the film ($\varepsilon_r = 15.6$ [40]), ε_0 is the vacuum permittivity, e is the electron charge, N_A is the acceptor density for *p*-type passive film, N_D is the donor density for *n*-type passive film, E is the applied potential, E_{FB} is the flat-band potential, k is the Boltzmann constant, and T is the temperature in Kelvin.

According to Eqs. (7) and (8), N_A and N_D of passive films can be calculated from the slope of the plots of C_{SC}^{-2} versus E :

$$N_A = -\frac{2}{\varepsilon_0 \varepsilon_r e} \left(\frac{dC^{-2}}{dE} \right)^{-1}, \quad (7)$$

$$N_D = \frac{2}{\varepsilon_0 \varepsilon_r e} \left(\frac{dC^{-2}}{dE} \right)^{-1}. \quad (8)$$

The Mott–Schottky plots of the passive films for Fe-based amorphous alloys at a measurement frequency of 10^3 Hz are illustrated in Fig. 5. The curves can be divided into three parts, namely P1 (the part with a negative slope), P2 (the part with a narrow potential plateau, where the electronic band structures of the films are called “flat-band” condition), and P3 (the part with a positive slope). P1 and P3 parts indicate the *p*-type and *n*-type semiconducting behaviour of the passive film, respectively. Mott–Schottky plots illustrate that the passive film of Fe-based amorphous alloys formed in acetic acid solution possesses a dipolar (*p*–*n*) semiconducting characteristic separated by the flat-band potential situated at around 0.50–0.60 V,

Fig. 5 Mott–Schottky plots of passive films formed on different W-containing Fe-based amorphous alloys after immersion in 1 mol/L acetic acid solution for 120 h at a measurement frequency of 10^3 Hz

where predominant electronic defects establish the transition between *p*-type and *n*-type semiconductivities [41]. Table 2 shows the influence of W content on the mean flat-band potential ($\overline{E_{FB}}$), N_A , and N_D calculated from the Mott–Schottky results. As the W content increases, $\overline{E_{FB}}$ becomes anodic, while both N_A and N_D dramatically decrease, indicating a less defective and highly protective passive film [10]. Furthermore, the conductive potential range (approximately the range of constant capacitance) significantly decreases with increasing W content (Fig. 5), implying W addition can improve the resistance of the passive oxide films [33]. Consequently, W addition can improve the stability and resistance of the passive films and thus enhance the corrosion resistance of Fe-based amorphous alloys.

The value of i_{pass} for Fe-based amorphous alloys in acetic acid solution is lower than that of the stainless steel [2, 42]. N_A and N_D of Fe-based amorphous alloys in acetic acid solution are in the order of 10^{18} cm $^{-3}$, which are much lower than those of the stainless steel and crystalline Fe–Cr alloys ($10^{20} \sim 10^{21}$ cm $^{-3}$) [43, 44]. Furthermore, Fe-based amorphous alloys exhibit better pitting resistance than stainless steel in the presence of inorganic acids and salts [16, 45]. Hence, these phenomena indicate the superior corrosion resistance and potential application of Fe-based amorphous alloys in complex engineering acetic acid-corrosive environments.

3.3 Angle-Resolved XPS Analysis

Angle-resolved XPS analyses for Fe $_{47}$ Cr $_{20}$ Mo $_{10}$ C $_{15}$ B $_6$ Y $_2$ and Fe $_{41}$ Cr $_{20}$ Mo $_{10}$ W $_6$ C $_{15}$ B $_6$ Y $_2$ amorphous alloys were conducted to distinguish the contribution of W addition on the chemical ingredient, oxide layer thickness, and valence electron state of passive film.

Figure 6 shows the XPS spectra of the passive films at the emission angle of 45°, and the predominant peaks are marked. The XPS spectra indicate the presence of Fe, Cr, Mo, B, C, Y, and O in the passive films. According to the peak intensity, the dominant components of the passive films are Fe, Cr, and Mo. The peak corresponding to W 4f is presented for Fe $_{41}$ Cr $_{20}$ Mo $_{10}$ W $_6$ C $_{15}$ B $_6$ Y $_2$ alloy, illustrating that W is related to the formation of the passive film.

Table 2 $\overline{E_{FB}}$, N_A , and N_D of passive films calculated from the Mott–Schottky plots

W addition (at.%)	$\overline{E_{FB}}$ (V)	N_A (10^{18} cm $^{-3}$)	N_D (10^{18} cm $^{-3}$)
$x = 0$	0.54 ± 0.01	3.38 ± 0.23	4.29 ± 0.11
$x = 2$	0.56 ± 0.01	1.39 ± 0.21	1.34 ± 0.13
$x = 4$	0.60 ± 0.04	0.60 ± 0.07	1.01 ± 0.01
$x = 6$	0.62 ± 0.01	0.47 ± 0.01	0.44 ± 0.14

Fig. 6 XPS spectra of the passive films on $\text{Fe}_{47}\text{Cr}_{20}\text{Mo}_{10}\text{C}_{15}\text{B}_6\text{Y}_2$ and $\text{Fe}_{41}\text{Cr}_{20}\text{Mo}_{10}\text{W}_6\text{C}_{15}\text{B}_6\text{Y}_2$ amorphous alloys formed in 1 mol/L acetic acid solution for 120 h at the emission angle of 45°

The XPS spectra of dominant constituents (i.e. Fe 2p, Cr 2p, Mo 3d, and W 4f) at the emission angle of 45° are depicted in Fig. 7. All of these spectra show a doublet structure due to the multiple splitting. The Fe 2p spectrum comprises the $2p_{1/2}$ and $2p_{3/2}$ peaks of metallic Fe^0 , Fe^{2+} oxide, and Fe^{3+} oxide. The Cr 2p spectrum represents the $2p_{1/2}$ and $2p_{3/2}$ peaks of metallic Cr^0 , Cr^{3+} oxide, and Cr^{6+} oxide. The Mo 3d spectrum shows the $3d_{3/2}$ and $3d_{5/2}$ peaks of metallic Mo^0 , Mo^{4+} oxide, and Mo^{6+} oxide. For $\text{Fe}_{41}\text{Cr}_{20}\text{Mo}_{10}\text{W}_6\text{C}_{15}\text{B}_6\text{Y}_2$ alloy, the W 4f spectrum consists of the $4f_{5/2}$ and $4f_{7/2}$ peaks of metallic W^0 , W^{4+} oxide, and W^{6+} oxide.

The contributions in the Fe 2p, Cr 2p, Mo 3d, and W 4f ionisations were qualified by peak fitting. The relative content of each ionised state was estimated from the integrity of the peak area of the individual constituent. The fitting results (shown in Table 3) suggest that W addition could modify the ionisation distribution of the Fe, Cr, and Mo constituents. Fe and Cr are more sensitive to W addition than Mo. With the addition of 6 at.% W, the relative contents of Fe^{3+} and Cr^{3+} oxides increase rapidly from 22.38 and 74.21 to 81.91 and 87.94%, respectively. Meanwhile, the relative contents of metallic Fe^0 , metallic Cr^0 , Fe^{2+} oxide, and Cr^{6+} oxide decrease with increasing amount of W added. The influence of W addition on the ionisation contribution of the Mo constituent is smoother than that of other elements. The relative content of metallic Mo^0 decreases, whereas the relative contents of Mo^{4+} and Mo^{6+} oxides slightly increase with the addition of 6 at.% W.

Adding W to Fe-based amorphous alloy promotes the formation of $\text{Fe}^{3+}/\text{Cr}^{3+}/\text{Mo}^{6+}$ oxides, particularly Fe^{3+} oxide. Fe^{3+} oxide exhibits high chemical stability, Cr^{3+} oxide has a broad range of acid stability and self-repair capability [46, 47]. Mo^{6+} ions can eliminate the “active sites” or “micro-pits” in the passive layer to enhance the pitting resistance [48, 49]. As shown in Table 3, the

dominant oxide of Mo in the passive film is Mo^{4+} oxide. In contrast to Mo, W is mostly in the form of W^{6+} oxide. This phenomenon reflects the superior chemical stability of W^{6+} oxide in acetic acid solution compared with that of Mo^{6+} oxide, similar to that in acidic sulphate solution [50]. Therefore, the modified chemical ingredient caused by W addition favours the formation of a stable and compact passive film to enhance uniform and pitting corrosion resistance.

Quantitative comparison of oxide composition and thickness was conducted based on the peak fitting results of XPS spectra at various emission angles to investigate the influence of W addition on the thickness of the passive oxide layer. The XPS results of Fe 2p, Cr 2p, Mo 3d, and W 4f at four emission angles of 0° , 15° , 30° , and 45° are illustrated in Fig. 8. According to Eq. (1), the thickness of different oxide layers can be calculated from the quantitative analysis of oxide and metal contributions. The final calculation results are listed in Table 4. The oxide layers possess a mixed stacking pattern, and the total thickness of the passive film is not simply the sum of each oxide layer [15, 51]. The thickness of the Fe and Cr oxide layers significantly increases with adding 6 at.% W, but that of the Mo oxide layer remains relatively constant. Hence, W addition can increase the average thickness of the passive film mainly by thickening the Fe/Cr/W oxide layers.

The effect of W addition on the passive films was also analysed in terms of valence electrons. The binding energy of the valence electrons around the Fermi level (labelled by the dash line in Fig. 9) is lowest among all valence electrons. Moreover, the binding energy of transfer charges is minimal among all valence electrons in oxide layers. Thus, the valence electron peak around the Fermi level is related to the density of transfer charges [52]. Substantially, the electrochemical corrosion process is the exchange transport of valence electrons among atoms or ions [53]. The low state density of valence electrons around the Fermi level implies high resistance of the oxide layer to impede the exchange of valence electrons during electrochemical corrosion. As shown in Fig. 9, the small state density of valence electrons around the Fermi level for $\text{Fe}_{41}\text{Cr}_{20}\text{Mo}_{10}\text{W}_6\text{C}_{15}\text{B}_6\text{Y}_2$ alloy at any emission angle reflects the higher pitting and uniform corrosion resistance than that for $\text{Fe}_{47}\text{Cr}_{20}\text{Mo}_{10}\text{C}_{15}\text{B}_6\text{Y}_2$ alloy.

4 Discussion

4.1 Semiconducting Property of Passive Films

Passive oxide films formed on metallic surfaces are extrinsic semiconductors because the oxides exhibit imperfect crystallography, donor or acceptor defects,

Fig. 7 XPS spectra separated using asymmetric Gaussian–Lorentzian mixed curve fitting of passive films formed on $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ amorphous alloys immersed in 1 mol/L acetic acid solution for 120 h at the emission angle of 45° : **a** $x = 0$ at.%, Fe 2p; **b** $x = 6$ at.%, Fe 2p; **c** $x = 0$ at.%, Cr 2p; **d** $x = 6$ at.%, Cr 2p; **e** $x = 0$ at.%, Mo 3d; **f** $x = 6$ at.%, Mo 3d; **g** $x = 6$ at.%, W 4f

Table 3 Ionisation contribution for each constituent in $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_xC_{15}\text{B}_6\text{Y}_2$ ($x = 0$ and 6 at.%) amorphous alloys at the emission angle of 45°

Ionised contribution (area%)		W addition (at.%)	
		$x = 0$	$x = 6$
Fe	Fe^0	30.26 ± 0.33	15.23 ± 0.16
	Fe^{2+}	47.36 ± 0.51	2.86 ± 0.03
	Fe^{3+}	22.38 ± 0.24	81.91 ± 0.86
Cr	Cr^0	10.29 ± 0.84	1.14 ± 0.01
	Cr^{3+}	74.21 ± 6.08	87.94 ± 0.91
	Cr^{6+}	15.50 ± 1.27	10.62 ± 0.11
Mo	Mo^0	36.24 ± 0.36	32.50 ± 3.04
	Mo^{4+}	36.53 ± 0.37	37.56 ± 2.43
	Mo^{6+}	27.23 ± 0.27	29.94 ± 2.44
W	W^0	–	30.17 ± 0.33
	W^{4+}	–	18.50 ± 0.20
	W^{6+}	–	51.33 ± 0.56

which distinguish these films as *n*-type or *p*-type semiconductors [54, 55]. As shown in Fig. 5, the capacitance responses reveal that the passive films possess a conjunction of *p*–*n* semiconductors separated by the flat-band potential. The increase in capacitance at applied potentials lower than the flat-band potential is attributed to the increased vacancy concentration in the valence band induced by anion adsorption. The decrease in capacitance at applied potentials is associated with a reduced donor density and a thick electron-depleted layer in the film/electrolyte interface. Moreover, the range of constant capacitance around the flat-band potential is attributed to the exhaustion of all donors in the film [35]. These results are consistent with the electronic band structure model proposed for passive films formed on stainless steel in borate buffer solution [56]. Hence, the passive film behaves as *p*-type and *n*-type semiconductors at potentials lower and higher than the flat-band potential, respectively.

In general, E_{FB} depends on pH and potential, whereas the anodisation of $\overline{E_{\text{FB}}}$ with W addition may be due to the differences in the affinity of absorption or adsorption of the anions on the passive films [57, 58]. As shown in Table 3, adding W does not change the semiconductor type, because W element can neutralise the dopant and induce a potential-dependent charge density. Essentially, the acceptors or donors in passive layers are defects, e.g. cation vacancies, anion vacancies, and cation interstitials. Higher N_{A} and N_{D} indicate more nonstoichiometric defects in the space charge region [59, 60]. Thus, W addition is beneficial to the stability of passive film of double passive layers. Similar effect of Y element on N_{A} and N_{D} for Fe-based amorphous alloys has also been reported [10]. Besides, the narrow conductive potential range with increasing W content

suggests the improved resistance of the passive films. Therefore, the stability and corrosion resistance of the passive films can be improved by modifying their semi-conducting property via W addition.

4.2 Doping Effect of W on the Chemical Characteristics of Passive Films

The distribution of each metallic cation in the passive film can be determined based on the relative amounts of cations in various states [61]. For example, the relative ratio of $\text{Cr}^{6+}/\text{Cr}^{3+}$ at a low emission angle is smaller than that at a high emission angle, illustrating the enrichment of high oxidation states (Cr^{6+} oxide) in the outer region of passive film. Therefore, the duplex membrane schematic of passive film formed on W-containing Fe-based amorphous alloys can be drawn according to the fitting results of Fe 2*p*, Cr 2*p*, Mo 3*d*, and W 4*f* spectra at varied emission angles. The cationic valence distributions in duplex passive layers have been analysed, and it can be concluded that the chemical characteristics of passive layers vary with alloys and solutions [62–64]. With regard to the duplex film in Fig. 10, the inner layer mainly comprises $\text{Fe}^{2+}/\text{Cr}^{3+}/\text{Mo}^{4+}/\text{W}^{4+}$ oxides, and $\text{Fe}^{3+}/\text{Cr}^{6+}/\text{Mo}^{6+}/\text{W}^{6+}$ oxides are dominantly located at the outer layer of the passive film. Given the enrichment of Fe^{3+} and Cr^{3+} oxides, the outer and inner layers exhibit *n*-type and *p*-type semiconductivities, respectively [33, 35]. Mo^{6+} and W^{6+} oxides are mainly located at the defective outer layer to prevent pitting dissolution, and W^{6+} oxide exhibits the higher stability than Mo^{6+} oxide [65, 66]. Therefore, the cation selective distribution of passive layers is considered to be largely responsible for the enhancement of corrosion resistance.

As shown in Fig. 7 and Table 3, adding W promotes the formation of $\text{Fe}^{3+}/\text{Cr}^{3+}/\text{Mo}^{6+}$ oxides, which can be explained in terms of the charge neutrality condition within the passive film and the stability of oxides [67]. Incorporation of W^{6+} or W^{4+} into Fe^{2+} oxide by substituting Fe^{2+} causes excess positive charges in the films. Therefore, the chemical composition of oxides is thermodynamically inclined to $\text{Fe}^{3+}/\text{Cr}^{3+}/\text{Mo}^{6+}$ oxides to maintain the relative charge neutrality and high stability of the oxide layers. Consequently, angle-resolved XPS analysis shows that W addition can thicken the passive film by changing the kinetics of anodic dissolution and passive film formation, which is consistent with the reports of Habazaki et al. [23, 68].

4.3 Relationship Between the Corrosion Behaviour and Characteristics of Passive Films

The outstanding corrosion resistance of amorphous materials is mainly influenced by the stability of a uniform

Fig. 8 XPS spectra of the passive film for Fe-based amorphous alloys at varied emission angles: **a** $x = 0$ at.%, Fe 2p; **b** $x = 6$ at.%, Fe 2p; **c** $x = 0$ at.%, Cr 2p; **d** $x = 6$ at.%, Cr 2p; **e** $x = 0$ at.%, Mo 3d; **f** $x = 6$ at.%, Mo 3d; **g** $x = 6$ at.%, W 4f

Table 4 Oxide layer thickness of passive films formed on W-containing Fe-based amorphous alloys

W addition (at.%)	Oxide layer thickness (nm)			
	Fe oxide layer	Cr oxide layer	Mo oxide layer	W oxide layer
$x = 0$	1.56 ± 0.02	3.82 ± 0.07	2.51 ± 0.03	–
$x = 6$	2.35 ± 0.09	6.25 ± 0.02	2.49 ± 0.07	2.61 ± 0.07

Fig. 9 Valence electron bands of the passive films formed on $\text{Fe}_{47-x}\text{Cr}_{20}\text{Mo}_{10}\text{W}_x\text{C}_{15}\text{B}_6\text{Y}_2$ ($x = 0$ and 6 at.%) amorphous alloys at varied emission angles **Fig. 10** Duplex membrane model of the passive film formed on Fe–Cr–Mo–W–C–B–Y amorphous alloys immersed in 1 mol/L acetic acid solution for 120 h

passive film. The charge transfer of passive films proceeds through conduction-band electrons or valence-band holes and governs the semiconducting properties of the passive film [35, 69]. Therefore, the relation between electrochemical behaviour and the semiconducting characteristics of passive films must be determined. The potentiodynamic polarisation and EIS curves in Fig. 3 indicate that adding W to Fe-based amorphous alloys can reduce passive current density and improve the charge transfer resistance in 1 mol/L acetic acid solution. Therefore, the corrosion resistance of Fe-based amorphous alloys is enhanced by W addition. Moreover, W addition shortens the conductive potential range and reduces the acceptor and donor densities, resulting in the formation of highly protective and stable passive films. As stated in the previous investigations, the varied chemical ingredients owing to Mo or W

addition favour the formation of a stable passive film barrier, which impedes ion migration [50, 70]. In this study, W addition enhances the corrosion resistance by forming highly stable $\text{Fe}^{3+}/\text{Cr}^{3+}$ oxides, the distribution of $\text{Mo}^{6+}/\text{W}^{6+}$ oxides at the outer layer, and reducing the state density of valence electrons around the Fermi level. Therefore, W addition has a beneficial effect on corrosion resistance by changing the semiconducting properties of oxides in the passive film, creating selective membranes and reducing the state density of valence electrons around the Fermi level.

5 Conclusions

1. W addition significantly increased the corrosion resistance of Fe–Cr–Mo–W–C–B–Y amorphous alloy in acetic acid solution. $\text{Fe}_{41}\text{Cr}_{20}\text{Mo}_{10}\text{W}_6\text{C}_{15}\text{B}_6\text{Y}_2$ alloy exhibited the lowest passive current density and the largest fitted charge transfer resistance in 1 mol/L acetic acid solution.
2. Mott–Schottky measurements indicated that passive films formed at the OCP exhibited dipolar (p – n) semiconducting characteristics separated by the flat-band potential. Partial substitution of W for Fe modified the semiconducting property of the passive films, namely W addition led to a narrow conductive potential range and a low disordered passive film by decreasing acceptor density (p -type inner layer) and donor density (n -type outer layer).
3. Angle-resolved XPS analysis revealed that W addition favoured the formation of $\text{Fe}^{3+}/\text{Cr}^{3+}/\text{Mo}^{6+}$ oxides, increased the average thickness of Fe/Cr/W-containing oxide layers, and reduced the state density of valence electrons around the Fermi level.
4. The duplex passive films formed on W-containing Fe-based amorphous alloy indicated that the inner layer mainly comprised $\text{Fe}^{2+}/\text{Cr}^{3+}/\text{Mo}^{4+}/\text{W}^{4+}$ oxides, and the outer layer dominantly included $\text{Fe}^{3+}/\text{Cr}^{6+}/\text{Mo}^{6+}/\text{W}^{6+}$ oxides. The selective distribution of metallic cations was propitious to reduce the number of defect sites and enhance the stability of the passive films, thereby enhancing the corrosion resistance of Fe-based amorphous alloys.

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