Corrosion Resistance and Electrochemical Behaviour of Amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ Alloy in Alkaline and Acidic Solutions

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Abstract

In this work, the corrosion behaviours of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its crystalline counterpart are studied in acidic, neutral, and alkaline solutions by scanning electron microscopy, electrochemical impedance spectroscopy, and potentiodynamic and potentiostatic polarization tests. X-ray photoelectron spectroscopy and scanning Kelvin probe are employed to characterize the alloy surface. The results show that the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy presents a better corrosion resistance compared to its crystalline counterpart, which is attributed to the uniform energy distribution of the atoms on the amorphous alloy surface, and this presents as a uniform electric potential map to effectively suppress the occurrence of the corrosion cell reaction.

Keywords Amorphous alloy · Corrosion · Electrochemical impedance spectroscopy · Potentiodynamic polarization · Scanning electron microscopy

1 Introduction

Recently, amorphous alloys have attracted increasing interest in the fields of national defence, aerospace, and high-end electronic industry. Compared to conventional crystal metallic materials, amorphous alloys possess many merits such as high strength [1, 2], soft magnetic property [3, 4], and corrosion resistance [5–8] in particular. For example, the tensile strength of Al-based amorphous alloys is 800 MPa and even reaches 1500 MPa in a partially crystalline state after an isothermal heat treatment [1]. Fe- and Co-based amorphous alloys with soft magnetic properties have been developed over the past decades, which now exceed those of the crystalline alloys based on Fe, Co, and Fe–Co. Using metallic glasses as catalysts, the higher activity can be achieved, which opens up a vista for catalyst development [9].

The most sensational property of amorphous alloys is their outstanding corrosion resistance, which may originate from the absence of grain boundaries. During the past 20 years, researchers have developed Fe- [10], Mg- [11], Zr- [12], and Ti-based [13] amorphous alloys, and their essences of corrosion prohibition have also been investigated. However, the intrinsic mechanisms for the corrosion resistance of amorphous alloys are still controversial. A main reason for better corrosion property of the amorphous $\text{Mg}_{65}\text{Cu}_{10}\text{Ag}_{15}\text{Y}_{10}$ alloy is ascribed to the homogeneity of structure and chemical composition, as reported by Rao et al. [2], while others have proposed that the admirable performance can be attributed to the certain chemical element, for example, Lu et al. [14] pointed out that the pit morphology of $\text{Cu}_x\text{Zr}_{100-x}$ ($x=40, 50$, and 60 at.%) metallic glasses is strongly dependent on the Cu concentration in the alloy. Through comparing the corrosion behaviours of amorphous $\text{Fe}_{66}\text{B}_{30}\text{Nb}_4$, $\text{Fe}_{56}\text{Cr}_{23}\text{Ni}_{5.7}\text{B}_{16}$, $\text{Fe}_{53}\text{Cr}_{22}\text{Ni}_{5.6}\text{B}_{19}$, and $\text{Fe}_{50}\text{Cr}_{22}\text{Ni}_{5.4}\text{B}_{23}$, Botta et al. [8] regarded the presence of Cr as the key factor, which can contribute to the formation of the passivation film on the surface, providing long-term protection. Li et al. [15] studied the influence of Ni additive on the structure and corrosion resistance of a series of $\text{Fe}_{73.5-x}\text{Ni}_x\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ ($x=0, 1, 2, 3$, and 4 at.%) amorphous ribbons in KNO_3 solution and found that the formation of a stable passivation film ensures a large passivation

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plateau. Besides these reports, some contradictory results on the corrosion resistance of amorphous alloys should not be overlooked. Schroeder et al. [16] found that the corrosion resistance of the amorphous $\text{Zr}_{42}\text{Ti}_{14}\text{Cu}_{13}\text{Ni}_{10}\text{Be}_{22}$ alloy is only slightly higher than that of its crystalline counterpart. Paschalidou et al. [17] reported that the ribbons containing crystals show a lower corrosion current and potential compared to the fully amorphous ribbons. By now, owing to the complex corrosion behaviours of alloys with various elements, no systematic investigation has been made to elucidate the corrosion resistance of amorphous alloys yet.

As one class of main industrial materials, Ni-based alloys show superior corrosion resistance in both acidic and neutral media and thus have been widely fabricated, such as $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_2\text{Sn}_3$ [18], $\text{Ni}_{53}\text{Nb}_{20}\text{Ti}_{10}\text{Zr}_8\text{Co}_6\text{Cu}_3$ [18], and $\text{Ni}_{57}\text{Ti}_{18}\text{Zr}_{20}\text{Si}_2\text{Sn}_3$ [19]. In this work, a novel amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, with good ability of glass forming and excellent mechanical properties, was selected to evaluate its corrosion properties. The corrosion behaviours of this amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ ribbon and its crystalline counterpart were studied using electrochemical methods. Furthermore, the corrosion mechanism was clarified through the surface analyses.

2 Experimental

2.1 Material and Sample Preparation

The amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy was prepared by melt spinning in an argon atmosphere with the dimensions of 2 mm in width and 18 μm in thickness. Figure 1 shows the images of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy obtained using an optical microscope (VHX-6000, Japan). The composition of the amorphous alloy was examined using an inductively coupled plasma spectrometer (ICP-MS, Agilent 7700, USA) and an atomic absorption spectrometer (AAS,

Agilent 240FS, USA). As listed in Table 1, the data obtained via ICP-MS and AAS show good consistency. The crystalline sample was prepared through the annealing of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy in vacuum at 973 K for 2 h, in which the temperature was determined by differential scanning calorimetry (DSC) traces. The dimensions of the alloy for electrochemical investigations were 10 mm $\times$ 2 mm $\times$ 0.018 mm, and the tested surfaces were ground with sandpapers and polished to 2.5 μm using diamond spray polishing compounds before testing.

2.2 Microstructure Characterization

The microstructure of the alloy was examined by using X-ray diffraction (XRD; D/Max-2500PC, Japan), transmission electron microscopy (TEM; FEI Tecnai G2 F20, USA), and scanning electron microscopy (SEM; FEI Inspect F50, USA). Thermal properties of the alloy were characterized by DSC (SETSYS Evolution 18, France) at a constant heating rate of 20 K min^{-1} from 298 K to 1773 K in a file://C:\Users\Leo\AppData\Local\youdao\dict\Application\7.5.1.0\resultui\dict\?keyword = nitrogen atmosphere.

2.3 Electrochemical Measurements

Electrochemical investigations of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and stainless steel were conducted using an electrochemical workstation (Parstat 4000A, USA) in hydrochloric acid solutions (pH = 1 and 3), distilled water (pH = 7), and sodium hydroxide solutions (pH = 11, 12, and 13). Potentiodynamic polarization and electrochemical impedance

Table 1 Composition of the sample examined via ICP-MS and AAS

	Ni	Cr	Si	Fe
ICP-MS	84.9	7.4	4.2	3.5
AAS	86.0	6.6	4.1	3.3

Fig. 1 Images of **a** shiny upper side of, **b** copper wheel side of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy obtained by an optical microscope

spectroscopy (EIS) were tested using a three-electrode system after the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and stainless steel were immersed in a solution at 25 °C for seven days. The EIS measurements were conducted at an open-circuit potential (OCP) over the frequency ranging from 100 kHz to 0.01 Hz at an applied sinusoidal perturbation of 10 mV after holding the OCP for 60 min, and the impedance data were fitted to the equivalent electric circuit using ZSimpWin software. The potentiodynamic polarization test was carried out at a potential sweep rate of 0.166 mV/s from $-0.25 V_{\text{OCP}}$ to $1.6 V_{\text{SCE}}$. The potentiostatic polarization for the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy was subsequently measured at $0.4 V_{\text{SCE}}$. After the potentiostatic polarization test, the surface morphology of the alloy was observed via SEM, and the chemical composition of the surface was examined using X-ray photoelectron spectroscopy (XPS; ESCALAB250, USA) with Ar-ion sputtering for 60 s. Electrochemical noise (EN) was conducted during 200 s at a sampling rate of 1 s to probe both the corrosion type and degree of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy in 0.1 M HCl. Fourier transform method was adopted to transform the potential and current noise data in the frequency domain.

2.4 Scanning Kelvin Probe

Potential maps of the amorphous alloy and its annealed sample were recorded using the scanning Kelvin probe (SKP) technique. The step-scan mode was employed with a step size of 20 μm , a scan area of 1000 μm^2 , and scan points of 51×51 .

3 Results and Discussion

3.1 Microstructure Characterization

Figure 2 displays the XRD patterns of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample. The former one consists of a broad peak without identified crystalline phases, which appear in the latter one of the annealed sample. Figure 3 shows the TEM images and the corresponding selected area electron diffraction (SAED) pattern of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, respectively. The amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy exhibits only a featureless amorphous phase, consistent with the XRD results.

3.2 Thermal Property

Figure 4 shows the DSC thermograms of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy. The crystallization temperature (T_x) is 738 K for the amorphous alloy, and three exothermic peaks appear when the temperature exceeds the value, indicating three crystallization stages at the temperatures of

Fig. 2 XRD patterns of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample

748 K, 801 K, and 869 K, respectively. The annealed temperature, 973 K, was thus selected after the third exothermic peak to produce the crystalline material.

3.3 Potentiodynamic Polarization Measurement

The $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and stainless steel (SS) samples (304 SS and 316 SS) were continuously soaked in solutions at room temperature for seven days, after which the potentiodynamic polarization was measured. Figure 5 shows the test curves of the samples. Their corresponding electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (I_{corr}), and corrosion rate (v_{corr}), are summarized in Table 2. In this work, v_{corr} was calculated via Eq. (1):

$$v_{\text{corr}} = \frac{mi_a}{nF\rho} \times 8.76 \times 10^4, \quad (1)$$

where m represents the relative atomic mass, i_a represents the anodic current density, n represents the number of electrons in the reaction, F represents the Faraday constant, and ρ represents the density of the working electrode. E_{corr} can be used to evaluate the material surface properties during the electrochemical process. In this work, E_{corr} of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy is more positive than that of its annealed sample, indicating the higher stability of the amorphous alloy than that of its crystalline counterpart. I_{corr} , another key parameter obtained from the potentiodynamic polarization curves, expresses the corrosion rate of the material. The amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy shows a lower I_{corr} value, demonstrating its better corrosion resistance. It is interesting to note that the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ material in the crystalline state exhibits the inferior corrosion performance

Fig. 3 TEM images and SAED patterns of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy

Fig. 4 DSC thermograms taken from the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy

compared to the stainless steel samples but offers superior corrosion resistance through the amorphization treatment.

3.4 EIS Measurement

EIS is a powerful method through which the charge transfer resistance (R_{ct}) of the electrode is measured, and the difficulty of the charge transfer between the electrode–electrolyte interface in an electrochemical reaction can be reflected. Figures 6, 7, and 8 show the impedance spectra of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and the stainless steel immersed in the solutions. From the Nyquist (Fig. 6) and Bode plots (Figs. 7, 8), the amorphous alloy presents the highest impedance values, which maintain a linear relationship near the low-frequency region at the pH values of 13, 12, 11, and

7. The phase angles of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy remain 90° from 1000 Hz to 0.01 Hz in Fig. 8a–d. The results indicate that the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy has the capacitive character and better corrosion resistance. The equivalent circuit for the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy tested at the pH values of 13, 12, 11, and 7 (Fig. 9) is composed of the resistance of the solution (R_s) and the resistance ($R(x_1)$) as well as the equivalent capacitance ($Q(x_1)$) of the oxidation film with a thickness of x_1 . The fitted values are listed in Table 3. The higher impedance of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy is attributed to the compact oxidation film that formed on the surface of the alloy, which is the main reason for the better corrosion resistance.

To verify the formation of the compact oxidation film only occurs in the NaOH solution, EIS was conducted for the amorphous alloy without being soaked (Fig. 10). The smaller phase in the Bode plots (Fig. 10b) of the sample indicates that the compact oxidation film is formed during soaking in the NaOH solution rather than storing in the air. In view of the inhomogeneity of the crystalline counterpart, an equivalent circuit was proposed to describe the electrochemical reaction of the annealed sample tested at the pH values of 13, 12, 11, and 7 (Fig. 11), which is composed of the solution resistance (R_s), the equivalent capacitance of the oxidation film (Q_{film}), the resistance of the pores distributed in the oxidation film (R_{pore}), the equivalent double capacitance between the interface of the solution and the film/alloy (Q_{dl}), and the charge transfer resistance of the film/alloy interface (R_{ct}). The fitted values are listed in Table 4.

An E –pH diagram was generated to intuitively depict the different corrosion behaviours between the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed counterpart (Fig. 12). A smaller corrosion region and a larger immunity region of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy

Fig. 5 Potentiodynamic polarization curves for 304 stainless steel, 316 stainless steel, amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, and its annealed sample at **a** pH=13, **b** pH=12, **c** pH=11, **d** pH=7, **e** pH=3, **f** pH=1

Table 2 Results of potentiodynamic polarization tests performed on the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and stainless steel samples

pH value	Measured parameter	Amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy	$\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy annealed at 973 K	304 SS	316 SS
13	E_{corr} (mV vs. SCE)	− 193	− 279	− 506	− 477
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.020	0.173	0.202	0.077
	v_{corr} (mm/y)	0.000213	0.001843	0.002995	0.000925
12	E_{corr} (mV vs. SCE)	− 163	− 232	− 394	− 405
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.016	0.200	0.265	0.091
	v_{corr} (mm/y)	0.000175	0.002131	0.003179	0.001088
11	E_{corr} (mV vs. SCE)	− 131	− 192	− 409	− 369
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.017	0.092	0.145	0.090
	v_{corr} (mm/y)	0.000181	0.000985	0.001548	0.001081
7	E_{corr} (mV vs. SCE)	− 44	− 188	− 443	− 419
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.016	0.338	0.063	0.034
	v_{corr} (mm/y)	0.000169	0.003596	0.000758	0.000406
3	E_{corr} (mV vs. SCE)	− 109	− 218	− 416	− 342
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.247	14.438	0.132	0.101
	v_{corr} (mm/y)	0.002639	0.153790	0.001583	0.001210
1	E_{corr} (mV vs. SCE)	− 160	− 197	− 309	− 374
	I_{corr} ($\mu\text{A}/\text{cm}^2$)	0.927	18.393	7.238	9.932
	v_{corr} (mm/y)	0.009872	0.195920	0.086861	0.119190

indicate its better corrosion resistance in comparison with the annealed one.

3.5 Potentiostatic Polarization Measurement

As an accelerating corrosion way, the potentiostatic polarization measurement was employed to assess the corrosion behaviours of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy in acidic and alkaline solutions. Figure 13 shows the test curves of the samples potentiostatically polarized at 400 mV in 0.1 M NaOH and HCl solutions. In 0.1 M NaOH solution, the current density of the annealed sample is much higher than that of the amorphous one in the first 200 s. After that, the current density of the annealed sample decreases slightly but can hardly become constant, which reflects its active surface in the polarization process. For the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, the current density shows a substantial reduction and is about 200 nA/cm² after testing for 3600 s, indicating a decrease in the corrosion rate in the polarization process. Figure 14a, b shows the surface morphologies of the amorphous and annealed $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ samples after testing at 400 mV for 3600 s in 0.1 M NaOH solution, respectively. Several solid particles are formed on the surfaces of both samples. The solid particles on the amorphous alloy are much denser than those on the annealed one, forming a compact oxidation film on the surface, which prevents further corrosion of the amorphous alloy.

Unlike the electrochemical behaviour of alloys in alkaline solutions, the corrosion current densities of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy in 0.1 M HCl solution are much higher than those in 0.1 M NaOH solution. In the HCl solution, the annealed sample also delivers more currents than the amorphous one, indicating the more serious corrosion of the annealed sample. The SEM images in Fig. 14c, d clearly show that although both samples corrode during the potentiostatic polarization test, the localized corrosion on the surface of the annealed sample is more serious.

3.6 XPS and ICP Tests

XPS analysis was conducted to examine the chemical composition of the surface oxidation film of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy after the potentiostatic polarization test conducted in 0.1 M NaOH at 400 mV for 3600 s. The XPS spectra of Ni 2p and O 1s after Ar-ion sputtering for 60 s are illustrated in Fig. 15. In the Ni 2p spectrum, the peaks of Ni 2p_{1/2} and 2p_{3/2} can be fitted by the deconvoluted peaks of Ni and Ni²⁺ (NiO and Ni(OH)₂). The peak in the O 1s spectrum represents the O^{2−} oxide state (NiO and Ni(OH)₂). Thus, the oxidation film on the surface of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy is mainly composed of Ni(OH)₂ and NiO. An element analysis of the solution after the potentiostatic polarization test was carried out via ICP. Figure 16a, b shows the element contents detected in 0.1 M NaOH and 0.1 M HCl solutions, respectively. Only

Fig. 6 Nyquist plots of 304 SS, 316 SS, amorphous alloy, and its annealed sample in soak solutions and corresponding fitted results of EIS data at **a** pH=13, **b** pH=12, **c** pH=11, **d** pH=7, **e** pH=3, **f** pH=1

a small amount of Si is identified in 0.1 M NaOH solution (Fig. 16a), while all four elements are apparently detected in the HCl solution (Fig. 16b). The element contents in the

solution soaked with the annealed sample surpass those with the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, which further

Fig. 7 Bode impedance magnitude plots of 304 SS, 316 SS, amorphous alloy, and its annealed sample in soak solutions and corresponding fitted results of EIS data at **a** pH=13, **b** pH=12, **c** pH=11, **d** pH=7, **e** pH=3, **f** pH=1

Fig. 8 Bode phase angle plots of 304 SS, 316 SS, amorphous alloy, and its annealed sample in soak solutions and corresponding fitted results of EIS data at **a** pH=13, **b** pH=12, **c** pH=11, **d** pH=7, **e** pH=3, **f** pH=1

Fig. 9 Equivalent circuit used to simulate the EIS data of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy tested at the pH values of 13, 12, 11, and 7

Table 3 Fitted values of the amorphous alloy

pH value of the soak solution	R_s ($\Omega \text{ cm}^2$)	$R_{(x1)}$ ($\Omega \text{ cm}^2$)	$R_{(x2)}$ ($\Omega \text{ cm}^2$)	$Q_{(x1)}$ ($\mu\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	$Q_{(x2)}$ ($\mu\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	$n_{(x1)}$	$n_{(x2)}$
13	10.60	2.32×10^{15}	3.35×10^{15}	15.79	3.78	1.000	0.917
12	8.43	3.46×10^{15}	4.63×10^{13}	6.92	1.54	0.814	0.978
11	7.75	2.77×10^{13}	1.40×10^7	3.13	4.40	0.948	0.549
7	14.63	9.67×10^{12}	1.12×10^6	4.28	1.49	0.938	0.921

Fig. 10 EIS results for the amorphous alloy in the air and soaked in the NaOH solution for 7 days

confirms that the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy owns better corrosion resistance than its annealed sample.

3.7 Electrochemical Noise Measurement

The local corrosion takes place on the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy polarized in 0.1 M HCl solution, as shown in Fig. 14c, d. To investigate the corrosion style and degree of the amorphous and crystalline samples in the acidic solution, EN

Fig. 11 Equivalent circuit used to simulate the EIS data of the annealed sample tested at the pH values of 13, 12, 11, and 7

measurement was conducted after the potentiostatic polarization test in the HCl solution at 400 mV for 3600 s, and the EN spectra are shown in Fig. 17. To interpret the EN data, the localized index (LI) is often used to describe the corrosion type during the electrochemical process [20], which is defined by Eq. (2):

$$LI = \frac{S_I}{I_{RMS}}, \quad (2)$$

where S_I represents the standard deviation of the noise current and I_{RMS} represents the root-mean-square of the noise current; S_I and I_{RMS} are pre-defined by Eqs. (3) and (4), respectively:

$$S_I = \sqrt{\frac{\sum_{i=1}^n (I_i - \bar{I})^2}{n - 1}}, \quad (3)$$

Table 4 Fitted values of the crystalline counterpart

pH value of the soak solution	R_s (Ω cm ²)	R_{pore} (Ω cm ²)	R_{ct} (Ω cm ²)	Q_{film} ($\mu\Omega^{-1}$ cm ⁻² s ⁿ)	Q_{dl} ($\mu\Omega^{-1}$ cm ⁻² s ⁿ)	n_{film}	n_{dl}
13	5.81	8.49×10^4	1.42×10^4	8.00	254.00	0.944	1
12	5.15	2.68×10^4	2.49×10^4	6.68	74.06	0.921	0.743
11	5.76	2.95×10^4	4.93×10^4	10.09	47.66	0.940	0.599
7	5.55	8.79×10^4	4.62×10^4	9.89	94.34	0.935	0.838

Fig. 12 E–pH diagram for **a** amorphous $Ni_{84.9}Cr_{7.4}Si_{4.2}Fe_{3.5}$ alloy, **b** annealed sample

Fig. 13 Potentiostatic polarization test curves in the double-logarithmic scale carried out in 0.1 M NaOH and HCl solutions at 400 mV

$$I_{\text{RMS}} = \sqrt{\overline{I_i^2}}, \quad (4)$$

where I_i and $\bar{I}$ are the transient and average values of the noise current, respectively, and n is the total number of the sampling points.

It has been generally recognized that the localized corrosion arises when the value of LI is close to 1, while proximity to 0 indicates the occurrence of uniform corrosion or passivation. For the identical corrosion style, a larger value of S_f means more severe corrosion of the material. In this work, the values of S_f , I_{RMS} , and LI are calculated, as listed in Table 5. The LI is almost 1, which denotes that the localized corrosion occurs on both the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample. Meanwhile, the larger S_f for the annealed sample infers that the corrosion resistance of the amorphous material reduces dramatically as a result of crystallization, corroborating the observations from the SEM images in Fig. 14c, d.

In this study, power spectral density (PSD) deduced from the EN raw data by Fourier transformation [21, 22] was adopted to further identify the corrosion behaviours of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample in 0.1 M HCl. Generally, the localized corrosion occurs when the slope of the PSD curve exceeds -20 dB/decade, while either uniform corrosion or passivation occurs when the slope remains below -20 dB/decade. Figure 18 shows the potential PSD curves based on the data in Fig. 17d, h. The slopes of the PSD curves of the amorphous

Fig. 14 SEM images of the amorphous alloy and its annealed sample after potentiostatic polarization tests at 400 mV for 3600 s. **a** Amorphous alloy in 0.1 M NaOH; **b** annealed sample in 0.1 M NaOH; **c** amorphous alloy in 0.1 M HCl; **d** annealed sample in 0.1 M HCl

Fig. 15 XPS spectra of **a** Ni 2p, **b** O 1s recorded from the oxidation film formed on the amorphous alloy with Ar-ion sputtering for 60 s

Fig. 16 Element analysis of the solution after the potentiostatic polarization at 400 mV in **a** 0.1 M NaOH solution, **b** 0.1 M HCl solution

$\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample are -15.55 and -5.88 dB/decade, respectively, both of which exceed the threshold of -20 dB/decade. The results indicate that the localized corrosions occur on both surfaces of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample. In addition, the slope of the PSD curve of the annealed sample is larger than that of the amorphous alloy, indicating the more severe localized corrosion on the annealed sample surface. These results confirm the conclusion that the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy has better corrosion resistance than its annealed sample in 0.1 M HCl.

3.8 SKP Measurement

The surface potential distribution of the $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy was probed via SKP. Figure 19 presents the 3D

potential maps, from which few potential fluctuations of the amorphous alloy can be observed, inferring that the surface potential distribution might play an essential role in causing the different corrosion resistances between the amorphous and the crystalline materials.

The main difference between the amorphous alloy and its crystalline counterpart is actually the uniformity degrees in structure and chemical property. The former exhibits the homogeneity, but the latter has the heterogeneity. Crystalline defects in the annealed sample, such as grain boundaries and dislocations, ordinarily possess more activity than the matrix in virtue of high-energy atoms. Furthermore, the energy of the atoms on the surface of the amorphous alloy is so well distributed that no areas with high energy can induce corruptions. For the crystalline counterpart, on the contrary, the energy distribution is non-uniform, as shown

Fig. 17 EN spectra of **a–d** amorphous alloy, **e–h** its annealed sample in 0.1 M HCl

Table 5 Values of S_I , I_{RMS} , and LI after the potentiostatic tests of the amorphous $Ni_{84.9}Cr_{7.4}Si_{4.2}Fe_{3.5}$ alloy and its annealed sample in 0.1 M HCl at 400 mV for 3600 s

	Amorphous alloy	Annealed sample
Solution system	0.1 M HCl	
S_I (nA)	0.19422	0.3784
I_{RMS} (nA)	0.19427	0.3785
LI	1	1

in Fig. 20. The energy of the atoms at the grain boundaries or defects exceeds that of the atoms on the other regions, resulting in the reduction in reaction activation energy when the electrochemical reaction occurs. Consequently, the non-equalizing energy distribution makes the crystal alloy prone to corrosion.

Form the literature, few investigations have been conducted for the corrosion behaviours of the amorphous alloy and its crystalline counterpart in alkaline and acidic solutions simultaneously. In the alkaline solution, both the amorphous $Ni_{84.9}Cr_{7.4}Si_{4.2}Fe_{3.5}$ alloy and its crystalline counterpart show excellent corrosion resistance. A much denser oxidation film is formed on the surface of the amorphous alloy, enhancing the corrosion resistance. In the acidic solution, various degrees of localized corrosions occur on the alloys. For the amorphous alloy, the energy of the atoms is uniformly distributed on the surface so that no corrosion can easily occur. In contrast, due to the high energy of the atoms at the grain boundaries and the defects of the crystalline material, the localized corrosion preferentially occurs at the grain boundaries and defects. Thus, the localized corrosion

Fig. 18 Potential PSD curves of **a** amorphous alloy, **b** annealed sample after the potentiostatic test in 0.1 M HCl at 400 mV for 3600 s

Fig. 19 SKP 3D potential maps of **a** amorphous alloy, **b** its annealed sample

Fig. 20 Potential energy curves in the reaction of the amorphous alloy and its crystalline counterpart

area on the crystalline counterpart of the amorphous alloy is large, as shown in the SEM image in Fig. 14d.

4 Conclusions

In this work, the corrosion behaviour of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy has been investigated in alkaline and acidic solutions through electrochemical, optical, and surface analysis methods. To evaluate the corrosion resistance of this novel amorphous nickel-based material, the electrochemical behaviours of the crystalline counterpart of the amorphous alloy along with 304 and 316 stainless steels have been compared. The results are summarized as follows:

1. Substantially different corrosion resistance is discovered between the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy and its annealed sample in alkaline and acidic solutions. In the alkaline solution, a compact oxidation film is formed on the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy, which may provide long-term protection. In the acidic solution, more severe localized corrosion occurs on the surface of the annealed sample than that of the amorphous alloy.
2. An opinion is proposed to elucidate the essence of the preminent protection of the amorphous alloy. The uniformly distributed energy of the atoms on the amorphous alloy surface, which presents as a uniform electric potential map, can effectively suppress the occurrence of the corrosion cell reaction. In contrast, the higher energy of the atoms at the grain boundaries or defects on the crystalline counterpart supplies an adequate driving force to induce corrosion.
3. The corrosion resistance of the amorphous $\text{Ni}_{84.9}\text{Cr}_{7.4}\text{Si}_{4.2}\text{Fe}_{3.5}$ alloy surpasses that of 304 and 316 stainless steels in this work but becomes inferior once undergoing crystallization.

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