

Corrosion Resistant Nanostructured Eutectic High Entropy Alloy

S. Shuang¹, Z.Y. Ding¹, D. Chung¹, S.Q. Shi², Y. Yang^{1,3,*}

¹. Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Kowloon Tong, Kowloon, Hong Kong, China

². Department of Mechanical Engineering, Faculty of Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

³. Department of Materials Science and Engineering, College of Engineering, City University of Hong Kong, Kowloon Tong, Kowloon, Hong Kong, China

* corresponding author. YY (yonyang@cityu.edu.hk)

Abstract

In this work, we developed a nanostructured eutectic high entropy alloy (EHEA) of composition FeCrNiCoNb_{0.5} (atomic %). Due to the formation of a compact amorphous high entropy passive film and the two-phase nanostructure, our EHEA exhibits unique combination of a low corrosion current **density**, a large passivation region and a superior repassivation ability in 1 M NaCl, outperforming the variety of conventional alloys and other high entropy alloys hitherto reported. The outcome of our research suggests that the notion of EHEAs could be explored to design corrosion resistant chemically complex alloys.

Keywords: A. High entropy alloy; C. Passivity; C. Repassivation; C. Pitting corrosion

1. Introduction

Corrosion has been a critical issue in the development of new structural materials, particularly metallic materials, because it poses a threat to the proper use of those materials by accelerating their failure during service time. As a consequence, if not mitigated, corrosion could cause significant economic loss, environmental damage and even human injury or death [1,2]. Therefore, understanding the corrosion behavior and the development of corrosion-resistant materials are of great importance. As of today, a great number of corrosion resistant alloys have been developed [3–11], such as stainless steel [3–5], aluminum alloys [6–9] and titanium alloys [10,11]. Among these alloys, 304 stainless steel (SS) has been widely used in many applications due to its excellent corrosion resistance [12–14], high strength and ductility [15,16]. These conventional alloy systems were usually designed based on the notion of minor alloying for enhanced corrosion resistance, i.e., the addition of minor elements, such as Cr, Ni, Al, to one or two base elements [17–19]. These minor elements play a vital role in improving the corrosion resistance of the alloys by forming compact, protective oxide films. This paradigm of alloy design has been adopted for centuries.

In contrast, the idea of high entropy alloys (HEAs) [20–22] or multi-principal element alloys [23–25], which was proposed by Yeh et al. in 2004 [26], offers a new route to design chemically complex alloys. Compared to conventional alloys, HEAs contain five or more principal elements in approximately equal atomic ratios [27], which have attracted tremendous research interest because of their excellent physical properties, such as high hardness and strength [28,29], good thermal stability [30] and good resistance to wear [31], corrosion [32–34] and high temperature oxidation [35,36]. As a result, HEAs are usually considered to be an engineering material with a great potential in various industrial applications, such as aero-engine [37], superconductor [38], and nuclear reactor [39].

The corrosion resistance of some HEAs, particularly the FeCrCoNi alloy system, has recently been explored [20,32,40–50]. For example, Hsu et al. [43] reported that the FeCrCoNi HEA, which was of a single-phased face centered cubic (FCC) structure, exhibited a better pitting corrosion resistance than the 304L stainless steel because of its high Cr content although the strength of the single phase FCC FeCrCoNi was rather low (~130 MPa) [51,52]. To improve the mechanical properties of the FeCrCoNi HEA, some minor elements were added [53–59]. To name a few, Al works as a body centered cubic (BCC) stabilizer in the Al-Co-Cr-Fe-Ni alloy system, which can increase the overall strength of the alloy because of BCC precipitation [55].

However, the corrosion resistance of the FeCrCoNi HEA could be impaired significantly after alloying. Luo et al. reported that addition of Mn reduced the Cr content in the passive film on the Fe-Cr-Ni-Co-Mn HEA, which led to poor anti-corrosion performance [50]. Besides, excessive addition of Mo resulted in the precipitation of (Cr, Mo)-rich σ -phase, resulting in preferential dissolution of (Cr, Mo)-depleted phase in the Fe-Cr-Ni-Co-Mo HEA [60]. A similar behaviour was observed in the Al-Fe-Ni-Cr-Co-Ti-V HEA [61], i.e. when the V content was increased to a certain level, minor σ phases was formed, causing the alloy's corrosion resistance to deteriorate. Due to the positive enthalpy of mixing, segregation of Cu would occur in the Fe-Cr-Ni-Co-Cu HEA [43], thereby leading to a micro-galvanic driven dissolution and accelerated localized corrosion because Cu-rich regions tend to be electrochemically less noble than Cu-depleted regions. Also, the formation of (Al, Ni)-rich and Cr-depleted BCC phase in the Fe-Cr-Ni-Co-Al HEA is susceptible to the attack of corrosive ions [44,62], hence causing severe pitting corrosion. In general, it seems that the multi-phased HEAs are less corrosion resistant than single-phased HEAs. A similar behavior was also observed in conventional alloys [63–65].

In this work, we would like to study the corrosion resistance of a nanostructured eutectic high entropy alloy (EHEA) we recently developed, which has a chemical composition of FeCrNiCoNb_{0.5} (in atomic %) and comprises a lamellar nanostructure with FCC and Laves phase. Despite the high volume fraction (~ 50%) of the Laves phase, which is notoriously known for its low toughness (~1 MPa·m^{0.5}) [66,67], this nanostructured EHEA however displays an excellent combination of strength (~ 2.3 GPa) and fracture toughness (~15 MPa·m^{0.5}) at room temperature [68]. Therefore, this nanostructured EHEA has a good potential to be used as the next generation of structural materials, particularly for high temperature applications [21,69–71]. More interestingly, we would like to demonstrate that, in sharp contrast to the Fe-Cr-Ni-Co-Cu and Fe-Cr-Ni-Co-Al systems, our Fe-Cr-Ni-Co-Nb alloy exhibits a remarkable corrosion resistance and superior self-repair ability under cyclic potentiodynamic polarization.

2. Experimental

2.1 Sample preparation

The FeCrNiCoNb_{0.5} EHEA samples were prepared by arc melting using Fe, Cr, Ni, Co, Nb metals of high purity (99.95%) as raw materials. To ensure the chemical homogeneity, the alloy ingots were fully re-melted at least five times in a Ti-gettered argon atmosphere. The melt was subsequently cast into a water-cooled Cu mold (50×10×5 mm³). To study the microstructure effect, some as-cast samples were annealed at 1473 K (1200 °C) under the static argon atmosphere for six hours in a tube furnace followed by water quenching. Besides, commercial 304L stainless steel (SS) was employed as the reference material. All samples for electrochemical tests were cut into 10×10×3 mm³ bulks. Their surfaces were ground sequentially with SiC papers of up to 2500 grit and finally polished with 0.5 μm diamond powder. After that, these samples were cleaned with

deionized water and alcohol, and dried in cold air. Prior to electrochemical measurements, the samples were sealed in epoxy resin with only one exposed face of an area of 1 cm².

2.2 Microstructural analysis

Before the variety of corrosion experiments, the microstructure and chemical composition of the samples were analyzed by a scanning electron microscope (SEM, Quanta FEG450) equipped with an energy dispersive X-ray spectrometry (EDX) and also by transmission electron microscopy (TEM, JEOL JEM-2100F). In addition, X-ray diffraction (XRD, Rigaku SmartLab) using Cu K α radiation was performed for structural characterization.

2.3 Electrochemical corrosion measurements

Potentiodynamic polarization tests, cyclic polarization tests, and electrochemical impedance spectroscopy (EIS) were performed in a typical three-electrode cell, which consisted of the test sample as the working electrode, a saturated calomel reference electrode (SCE), and a carbon rod counter electrode. All potentials stated in this paper were measured against the SCE. The measurements were carried out in 1 M NaCl solution at 25 °C under atmospheric pressure, using the Vertex™ electrochemical workstation (Iviumstat Technology). The open circuit potential (OCP) was recorded for 1 hour to attain a steady potential prior to these tests. For potentiodynamic polarization measurements, each sample was scanned at a rate of 1mV/s from an initial potential of -0.3 V (vs. OCP) to a final potential of 1.3 V (vs. OCP). Cyclic potentiodynamic polarization (CPP) tests started at -0.2 V (vs. OCP) at the scanning rate of 1 mV/s towards a more positive potential until the current density reached a maximum value of 5 mA/cm². After that, reverse scan was started and terminated at the potential where the polarization began. EIS was performed at the corresponding OCP with the applied alternating current (AC) amplitude of 10 mV in the frequency

range of 100 kHz to 10 mHz. All the electrochemical tests were repeated at least 3 times to confirm the data reproducibility.

2.4 Characterization of the passivation film

To understand the mechanism of passivation, a potential of 0.6 V (vs. SCE) was first applied on our sample for 3 h to obtain a stable passive film. A cross-section thin foil containing the passive film was then prepared with the focused ion beam (FIB) technique (FEI Scios DualBeam). To protect the passive film, a Pt layer was deposited before FIB milling. The TEM image of the passive film was obtained with the transmission electron microscope (TEM, JEOL JEM-2100F) equipped with EDX. In addition, the Mott-Schottky (M-S) analysis was performed within the potential range from -0.6 VSCE to 0.2 VSCE in order to probe the semi-conductive property of the passive film. Before the capacitance measurements, the electrodes were initially pre-passivated at OCP for 3 h. The scanning rate was 10 mV/s at the AC voltage of 5 mV and the frequency of 1000 Hz.

2.5 Surface morphologies

To understand the mechanism of corrosion, the sample surface morphologies at several selected stages of the cyclic polarization test, were examined using SEM and atomic force microscope (AFM). To achieve high spatial resolution, a special AFM tip coated with a 1-nm sharp carbon nanotube was employed in this study [72]. The chemical composition of the corrosion products was also analyzed using EDX.

3. Results

3.1 Microstructural Characterization

[Figure. 1 \(a\)](#) shows the XRD pattern of the as-cast FeCrNiCoNb_{0.5} EHEA, which reveals that our EHEA is composed of a C14 Laves phase and a FCC phase. To characterize its microstructure,

the surface of one specimen was chemically etched and examined under SEM. As seen in Fig. 1 (b), a typical lamellar eutectic structure could be observed. Notably, because of the difference of the etching speed, the Lave phase was revealed as the bright regions (slow etching speed) while the FCC phase as dark regions (fast etching speed). According to these observations, the volume fraction of the Laves phase was estimated to be 51%, which is slightly higher than that of the FCC phase. TEM examinations were also performed [Fig. 1 (c)], which confirmed the crystalline structure of both phases through the selected area diffraction patterns (SAD), being consistent with the XRD result. As shown in Fig. 1 (c), the width of the lamellae varies between 80 nm and 150 nm regardless of the phase difference. The chemical compositions of the two phases were studied by EDS, according to which the FCC phase is Nb-lean while the Laves phase is Nb-rich, as listed in Table 1. Moreover, since the phase boundary is susceptible to a corrosion attack [73–75], we examined the interface between the FCC and Lave phase. As shown by the high-resolution transmission electron microscopy (HRTEM) image [Fig. 1 (d)], discrete atomic steps can be observed along the interface, which is the typical morphological feature of non-faceted eutectic growth. This behavior suggests a low entropy of fusion or a high entropy of solid solution during solidification of our EHEA [76].

3.2 Corrosion and passivation

In order to study the anti-corrosion behavior, potentiodynamic polarization curves of our EHEA were measured in 1M NaCl solution, which were compared afterwards to those obtained from 304 SS [Fig. 2 (a)]. Evidently, both alloys are able to passivate; however, the passivation region of our EHEA is much wider than that of the 304 SS in terms of the difference between the passivation breakdown potential (E_b) and the corrosion potential (E_{corr}). Here, it is worth mentioning that our EHEA and the 304 SS seemingly enter the stable passivation region directly

from the linear regime of E versus $\log(i)$ (or the so-called Tafel region [77]) in absence of an active-passive transition, in which E stands for the potential and i for the current density. This behavior suggests that the growth of the passivation film on both alloys is spontaneous at their corresponding corrosion potential [78,79], as seen in Fig. 2 (a).

Table 2 listed the various electrochemical parameters extracted from the polarization curves obtained from our EHEA and 304 SS, including not only E_b , E_{corr} and the passivation region ($E_b - E_{corr}$) but also the corrosion current density (I_{corr}). Apparently, the E_{corr} (-238 mV_{SCE}) and I_{corr} (24.29 nA/cm²) of our EHEA are comparable to those of the 304 SS ($E_{corr} = -196$ mV_{SCE} and $I_{corr} = 30.45$ nA/cm²). Since the corrosion current density is directly proportional to the corrosion rate [80,81], the similar corrosion current density indicates a similar corrosion rate between our EHEA and 304 SS when corrosion takes place at E_{corr} . More importantly, our EHEA exhibits a significantly higher E_b (976 mV_{SCE}), which is about three times of the 304 SS with $E_b = 346$ mV_{SCE}. Accordingly, the passivation region ($E_b - E_{corr}$) of our EHEA is much wider (1214 mV_{SCE}), which is nearly three times of that of the 304 SS (433 mV_{SCE}). Since the passivation region is usually associated with the stability of the passive film on a metal surface [82,83], the wide passivation region suggests a rather stable passive film on the surface of our EHEA.

For a comprehensive comparison, we extracted the corrosion parameters from the potentiodynamic polarization curves reported for a variety of HEAs [32,47,81,84–86] and conventional alloys [87–97] (Table 3). Note these corrosion parameters were all obtained in 1 M NaCl at room temperature and all the potentials listed in Tables 3 were converted to the potentials versus standard calomel electrode (SCE). Here, it should be pointed out that, among the alloys selected for comparison, only Co_{1.5}CrFeNi_{1.5}TiMo_x HEAs [32] exhibited an active-passive transition. Therefore, the passive region of the Co_{1.5}CrFeNi_{1.5}TiMo_x HEAs [32] was set as the

difference between the breakdown potential (E_b) and primary passivation potential (E_{pp}). In contrast, the passive region of the others was set as the difference between the breakdown potential (E_b) and the corrosion potential (E_{corr}).

Fig. 2 (b) compares the anti-corrosion properties of the variety of alloys in terms of $-\log(I_{corr})$ and the magnitude of the passive region. Evidently, our EHEA displays a very low corrosion current density and a wide passive region. Generally speaking, its performance is comparable to the best forming stainless steels but better than most conventional alloys, such as Al-, Ti- and Ni-based alloys [89,92–97], in terms of its unique combination of the corrosion current density and passive region. Notably, compared to the HEAs reported in the prior works [32,47,81,84–86], our EHEA exhibits the lowest corrosion current density, suggestive of a remarkably low corrosion rate.

To further characterize the corrosion properties, we performed EIS measurements for our EHEA and the 304 SS. As shown in Fig. 2 (c), both alloys exhibit a similar semi-circular type of Nyquist plot; however, the diameter of the semicircle for the EHEA is larger than that of the 304 SS, suggestive of a higher corrosion resistance of the EHEA [98]. As seen in the corresponding Bode plot, the $|Z|$ value of our EHEA is also higher than that of the 304 SS [Fig. 2 (d)], which further confirms the better corrosion resistance of EHEA. Notably, our EIS data can be fit well to the circuit model with one single time constant [the inset of Fig. 2 (c)], which consists of an electrolyte resistance (R_s), a polarization resistance (R_p), and a constant phase element (CPE) for a double layer capacitance. The admittance (Y) of CPE is expressed as $Y = Y_0(j\omega)^n$, where j is the imaginary number; ω is the angular frequency; Y_0 and n are the magnitude and exponential term of the CPE, which are frequency-independent parameters [99]. According to the literature [100–102], the CPE corresponds to an ideal capacitor for $n=0$ while to an ideal resistor for $n=1$. For the intermediate case of $0 < n < 1$, the value of the CPE can be correlated with the surface roughness.

The general trend is that the lower is the n value the rougher is the corresponding electrode surface [103].

Table 4 lists the fitted electrochemical parameters. The fitting quality is evaluated by the chi-squared (χ^2) values, which are of the order of 10^{-3} , and the error percentage corresponding to each component of the equivalent circuit (values given in Table 4) indicates a good mathematical fitting [104–106]. Interestingly, the n values of both 304 SS and EHEA are similar and close to unity. This indicates that both alloys behaved in the EIS tests in a manner akin to a capacitance with a rather smooth surface [81]. Furthermore, the fitted value of the electrolyte resistance (R_s) for both alloys is significantly smaller than that of the corresponding polarization resistance (R_p). This makes sense, since R_p , as strongly depends on the passive film, can be regarded as an indicator of the corrosion resistance of a material [50]. Both 304 SS and our EHEA possess good corrosion resistance. Since a larger R_p generally corresponds to a better corrosion resistance [107–109], our EHEA appears more corrosion resistant than 304 SS because of its higher R_p value. Again, this is in good agreement with the results obtained from potentiodynamic polarization.

3.3 Repassivation

Aside from regular potentiodynamic polarization, cyclic potentiodynamic polarization (CPP) was also performed to study the self-repairability of the passive film on our EHEA in the 1 M NaCl solution. As seen in Fig. 2 (e), positive hysteresis occurs in our EHEA when the potential is higher than 767 mV_{SCE} in the reverse scan, which is way above the corrosion potential ($E_{corr} = -232$ mV_{SCE}) detected in the forward scan and hence indicative of repassivation [110]. Apparently, the 304 SS does not show a prominent repassivation behavior in CPP. Table 5 details the potential parameters extracted from the CPP curves of the EHEA and 304 SS. Here, the corrosion potential (E'_{corr}) and breakdown potential (E'_b) determined from the CPP curves are similar to those from

the previous PD curves. Following the literature [111–113], the repassivation (or protection) potential (E_{rp}) is defined as the intersection of the forward and reverse scan while the pit transition potential (E_{ptp}) as the potential at which the anodic current density transitions to the cathodic current density. Compared to the 304 SS, our EHEA shows a considerably nobler E_{rp} and smaller $E'_b - E_{rp}$, indicative of less pitting propagation and excellent localized corrosion resistance [112–114]. Notably, the values of E_{rp} and E_{ptp} of the EHEA are much higher than the E_{corr} . This behavior suggests a remarkable self-repairability of the passive film formed on our EHEA [114,115].

3.4 Corrosion morphologies

Next, we examined the surface morphologies of the EHEA, as well as that of the 304 SS for a reference, at three selected time points on their respective CPP curves [a-f in Fig. 2 (e)]. This was done in an ex-situ manner, and the tests were deliverably stopped at the selected time points such that the sample surfaces could be examined with SEM and EDS [Figs. 3 (a)-(h)]. As seen in Figs. 3 (a) and (d), pitting could be observed on the surface of both the EHEA and 304 SS at the onset of trans-passivation. However, the average pit size on the EHEA surface is $\sim 1.5 \mu\text{m}$ and about 16 times smaller than the average size of the pits ($\sim 25 \mu\text{m}$) on the 304 SS surface. Interestingly, as the potential continued to increase, it seems that the FCC phase was selectively dissolved while the pits did not grow further on the EHEA surface [Figs. 3 (b)-(c)], implying that they could be metastable in nature [116,117]. In contrast, the pit size increased with the potential on the 304 SS surface and grew to $\sim 100 \mu\text{m}$ at $E = -197 \text{ V}_{\text{SCE}}$ [Fig. 3 (f)]. This behavior is consistent with our CCP results since large pits are difficult to be repassivated according to Refs [118,119]. In other words, the small pits on the EHEA surface is in accord with the noble repassivation potential and a good repassivation ability. Figs. 3 (g) and (h) show the corrosion products detected via EDS at the pit site on the EHEA [Fig. 3 (b)] and on the 304 SS [Fig. 3 (e)], respectively.

Evidently, the corrosion product in the pit of the EHEA is mainly metal oxide while that at the pit of the 304 SS contains not only metal oxide but also chloride. A similar phenomenon of Cl^- ion accumulation was reported in Ref. [105]. In general, the presence of Cl^- is commonly believed to catalyze and accelerate pitting corrosion [120–122].

4. Discussion

4.1 Passive film

To understand the mechanism underlying the excellent corrosion resistance, we first examined the surface of our EHEA. Fig. 4 (a) shows the cross-sectional TEM image of the EHEA sample, which was subject to a potential at $0.6 V_{\text{SCE}}$ in 1 M NaCl solution for 3 h. Evidently, one can observe three layers including a deposited Pt, a passive film, and the EHEA. As shown in the HRTEM image [Fig. 4 (b)], the thickness of the passive film is about 5-6 nm, which is comparable to that of the passive film (~ 3 nm) formed on the Fe-Cr alloy under the potential of $\sim 0.4 V_{\text{SCE}}$ [123,124]. Notably, this passive film is of an amorphous structure, as seen in the fast Fourier transform (FFT) image [the inset of Fig. 4 (b)]. Fig. 4 (c) shows the energy-dispersive X-ray spectrometer (EDS) line profiles obtained along the path as indicated by the yellow arrow in the cross-sectional TEM image. Based on the EDS results, it is clear that region 1 corresponds to our EHEA while region 2 to the surface passive oxide film, which consists of Cr, Ni, Co, Nb, Fe and O. To be consistent with the literature results [123,125], the boundary between region 2 and 3 is determined based on the full width at half maximum (FWHM) of the oxygen signal profile.

According to the EDS profile of O, we can determine that the thickness of the chemically complex or high entropy oxide film is ~ 6 nm, being consistent with the rough estimate of the film thickness made based on Fig. 4 (b). Interestingly, one can observe a 16-nm thick oxygen rich but metal depleted layer (region 3) next to the oxide film. According to Refs. [126–129], such an

oxygen rich layer is commonly observed on top of oxide films during passivation of metals, which could be attributed to the surface absorption of oxyhydroxide and/or water molecules in the outermost layers of the passive film [130–133]. Given the detected Fe and Cr elements and corrosive solution (neutral chloride solution), the oxyhydroxide could be a mixture of $\text{Cr}(\text{OH})_3$ and FeOOH [134]. In addition, it is worth mentioning that the presence of water molecules could weaken the metal signals in Region 3 because water molecules could remain adsorbed or bounded onto the alloy surface even under a ultrahigh vacuum, as discussed in [135,136]. Finally, region 4 corresponds to the Pt layer we deposited onto the EHEA sample for surface protection.

Apart from the chemical analyses, we also examined the topography of the EHEA surface with AFM, which was done in an ex-situ manner after the film was formed at the potential of 0.6 V_{SCE} in 1 M NaCl solution. As seen in Figs. 4 (e)-(f), nano-sized spikes with a height as large as 26 nm could be observed at numerous spots. In addition, surface cavities or valleys could be observed around these spikes. A similar phenomenon of nano-spike formation was reported in Refs [126–128], which was then attributed to oxyhydroxide aggregates. It is noteworthy that the average spike height is ~ 18 nm, which is in agreement with the thickness of region 3 estimated from Fig. 4 (b), thereby corroborating the idea that region 3 could result from surface oxyhydroxide aggregates.

Fig. 5(a) shows the cross-sectional TEM image of the EHEA sample, from which one can clearly see the passive films on the Laves and FCC phase. According to the results of elemental mapping [Figs. 5 (b)-(f)], there is no significant difference in the concentration of Fe, Cr, Ni, Co in the passive films on the FCC and Laves phase. However, it appears that the passive film on the Laves phase contains more Nb than that on the FCC phase [Figs. 5 (g)]. This could be due to the high Nb content ($=20.4$ at.%) in the Laves phase as opposed to the low Nb content ($=1.5$ at. %) in

the FCC phase. Please note that, as it is difficult to detect oxygen (O) with EDS because of its light weight [123], we do not show the result of elemental mapping for O here.

According to our EDS result (**Table 1**), the FCC phase contains 28.1 at.% Cr while the Laves phase contains 17.0 at.% Cr. According to Refs. [137,138], such high concentrations of Cr could promote the formation of passive films on both phases. However, in sharp contrast to the low concentration (1.5 at.%) of Nb in the FCC phase, the Laves phase contains 20.4 at. % Nb. According to Refs. [139,140], Nb is conducive to forming highly protective oxide films, being corrosion resistant even at very high oxidizing potentials. Furthermore, according to Kim et al. [151], the corrosion rate of binary Cr-Nb alloys is about four orders of magnitude lower than that of pure chromium. This suggests that a balanced concentration of Nb and Cr, as is the case for the Laves phase, could result in higher corrosion resistance in the passive film [141,142].

In general, passivation or repassivation can be attributed to the formation of an oxide passive film [143]. From a thermodynamic viewpoint, the driving force of repassivation is the reduction in the Gibbs free energy associated with oxide formation. The repassivation potential of the EHEA is 1008 mV_{SHE}, at which a stably growing pit or crevice corrosion ceases to grow [144]. Based on the Pourbaix diagrams for Fe, Cr, Ni, Co and Nb [145,146], we found that only the potential range for the passivation on Nb (from -500 mV_{SHE} to 1000 mV_{SHE} with pH 7) is in good agreement with the repassivation potential range of our EHEA. This finding suggests that the thermodynamic driving force for the repassivation on our EHEA is likely to be associated with the reduction in the Gibbs free energy associated with the formation of an Nb-containing oxide.

Furthermore, we carried out Mott-Schottky (M-S) experiments to study the semi-conductive behavior of the high entropy oxide film. Based on the well-established M-S relationship [147–149], the space charge capacitance (C_{sc}) can be related to the applied potential E as follows:

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon\varepsilon_0qN_q} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (1)$$

where ε is the film's dielectric constant, normally assumed to be 15.6 [150,151]; ε_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ F m}^{-1}$); q is the elementary charge ($-e$ for “hole” and $+e$ for “electron”); N_q is the charge carrier density (N_A for “acceptors” and N_D for “donors”); E_{fb} is the flat band potential; k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$); T is the absolute temperature and e is the electron charge ($1.6 \times 10^{-19} \text{ C}$). Note that N_q can be extracted from the slope of the linear portion of the experimental curve of $1/C_{sc}^2$ vs. E , while E_{fb} can be determined at $1/C_{sc}^2=0$.

Fig. 6 (a) shows the M-S plots obtained for the EHEA and 304 SS at the open circuit potential (OCP) in the 1 M NaCl solution for 3 h. The linear dependence of C_{sc}^{-2} on E is evident for the EHEA for $-0.46 \text{ V}_{\text{SCE}} < E < -0.03 \text{ V}_{\text{SCE}}$, and for the 304 SS for $-0.33 \text{ V}_{\text{SCE}} < E < 0.17 \text{ V}_{\text{SCE}}$. The positive slope for these two alloys indicates that both passivation films are of an n-type semiconductor; in other words, the number of electrons in the conduction band of the corresponding oxide is more than that of holes in the valence band. By comparison, the linear slope of the EHEA is larger than that of the 304 SS, therefore suggestive of a lower charge carrier density in the EHEA according to Eq. (1). Fig. 6 (b) compares N_D and E_{fb} obtained from the M-S plots between the EHEA and the 304 SS. Notably, the flat band potential E_{fb} for the passive film on the EHEA ($= -0.559 \text{ V}_{\text{SCE}}$) and 304 SS ($= -0.425 \text{ V}_{\text{SCE}}$) are more negative than the corresponding corrosion potential. Furthermore, the donor density of point defects in the high entropy oxide film on the EHEA is $4.48 \times 10^{20} \text{ cm}^{-3}$, which is around half of the donor density in the passive film on the 304 SS ($9.01 \times 10^{20} \text{ cm}^{-3}$) and two orders of magnitude smaller than the N_D ($\sim 10^{22} \text{ cm}^{-3}$) values reported for conventional passive films [152–154]. In general, oxygen vacancies facilitate electron

transfer during electrochemical reactions and, therefore, a high (low) donor density would accelerate (retard) the corrosion rate [149,155]. As such, the rather low donor density N_D indicates that the high entropy oxide film formed on the EHEA surface is less defective, more compact and protective, which explains the good corrosion resistance of the EHEA.

4.2 Nanostructure effect

In addition to the compact passive film, the nanostructure also plays a critical role in the excellent corrosion resistance of the EHEA. According to T. Okada [156,157], pit nucleation is essentially an event of electrochemical instability and originates from the coupling of local anodic sites in the presence of perturbations in an electric field and the concentration of attacking ions, such as Cl^- . In theory, the electrochemical instability takes place once the average spacing of the anodic sites (l) is larger than a critical wavelength (λ_c) of the perturbations, which can be calculated via $\lambda_c = 2\pi / k_c$, where k_c is the critical wave number of the perturbations. Based on the theoretical model of Okada [156,157], k_c can be expressed as

$$k_c = \frac{E_x}{2(1+z)\zeta} \left\{ h(W) + \sqrt{(h(W))^2 + 4(1+z)\zeta(az+m-\beta)W} \right\} \quad (2)$$

in which:

$$\zeta = zC_M / C_X \quad (3a)$$

$$h(W) = (az+m-\beta)W - z\zeta \quad (3b)$$

$$W = \frac{I_a}{FD_M C_X E_x \left(1 + \frac{\beta}{\alpha_f}\right)} \quad (3c)$$

where E_x = the electric field at the interface between the passive film and electrolyte, z = the charge of metal ion species, m = a constant related to the Cl^- concentration at the interface, C_M = the metal

ion concentration at the interface, C_x = the Cl^- concentration at the interface, α and β = the constants related to the energy profile in the metal dissolution reaction, I_a = the anodic current density, F = the Faraday constant, D_M = the diffusion coefficient of metal ions in the electrolyte, a_f = the transfer coefficient of donors in the passive film. According to the literature [156–158], we have $E_x \sim 10^8$ V/m, $m = 3$, $F = 96485$ C/mol, $D_M = 10^{-10}$ m²/s and $a_f = 0.3$ for a general metal corrosion process. For our EHEA, we approximately take $z \sim 2$ and can extract $I_a = 50$ A/m² based on the electrochemical tests. For simplicity, C_x is taken to be the concentration of Cl^- in solution ($\sim 10^3$ mol/m³). By integrating the anode current density with time, we can calculate the amount of electron loss during the oxidation of the EHEA, and therefore obtain the concentration of the dissolved metal ions $C_M \sim 0.56$ mol/m³ and $\zeta \sim 10^{-3}$. As a result, we estimate that the critical wavelength (λ_c) should be ~ 6 μm for our EHEA. In other words, if the average spacing (l) between the anodic sites on the surface of our EHEA was smaller (greater) than ~ 6 μm , pitting would be suppressed (facilitated).

As seen in Figs. 6 (a) and (g), at the beginning of transpassivation, a large number of distinct nano-spikes or protrusions, 4 to 8 nm high [Fig. 6(d)], can be observed over the whole surface of our EHEA. However, these protrusions ruptured [Fig. 6(g)] and broke into shorter pieces [~ 8 nm in Fig. 6 (d)] as the transpassivation continued. In principle, the transpassive potential at the surface accelerates corrosion reactions, leading to the rupture of protrusions and passivity breakdown [159,160]. As shown in Figs. 6 (b) and (h), when the current density reaches 5 mA/cm², all spikes and protrusions disappear on the EHEA surface. Meanwhile, the FCC phase dissolved and became 25 to 40 nm deeper than their neighboring Laves phase, the latter of which remained almost at the same height throughout the tests. This selective dissolution delivers a strong message that the FCC phase in our EHEA worked as the anodic sites..

Since the average spacing (l) of the FCC phase is ~ 100 nm, which is 60 times smaller than the estimated critical perturbation wavelength ($\lambda_c = 6 \mu\text{m}$), the pits on the EHEA surface cannot grow according to the model of Okada [156,157], which is in excellent agreement with our experimental observations. In other words, the pits observed on the EHEA can be all viewed as metastable in nature [Figs. 3 (a)-(c)]. Interestingly, when the scanning potential was reversed, nano-spikes appear again on the surface of the EHEA [Figs. 7 (c) and (i)], indicative of re-passivation. During this process, the FCC phases dissolved very slowly, as manifested by the slight change in their depths [Figs. 7 (f)]. Given the fine structure of our EHEA, the selective corrosion behavior of the FCC phase conforms more to a general corrosion process.

To further substantiate the nanostructure effect, we annealed the as-cast EHEA at 1473 K for six hours. As a result, the lamellar nanostructure coarsened and turned into a microstructure [Fig. 8 (a)]. As seen in Fig. 8 (b), the annealed EHEA exhibits a large passivation region ($E_b - E_{corr} = 1.2$ V) comparable with that of the as-cast one, which could be attributed to the formation of the compact passive high entropy oxide film. In the coarsened eutectic microstructure, the average spacing of the FCC phase is around 6~10 μm , which is slightly above the critical perturbation wavelength ($\lambda_c = 6 \mu\text{m}$). Consequently, stable pitting occurred in the annealed EHEA. This manifests as the considerably more negative E_{rp} , larger $E_b - E_{rp}$ and thus a generally poorer self-repairing ability on the cyclic potentiodynamic polarization curves [Fig. 8 (b)]. The surface morphology of the annealed EHEA was also examined with SEM at the point of re-passivation [b in Fig. 8 (b)]. As seen in Fig. 8 (c), the FCC phases corroded significantly and formed a local pit with the size of $\sim 15 \mu\text{m}$. The pit size is about ten times of the small metastable pits ($\sim 1.5 \mu\text{m}$) observed on the as-cast nanostructured EHEA, which indicates severe pit localization and, in turn, confirms the nanostructure effect on pitting nucleation. **Compared to metastable pits of a smaller**

size, larger stable pits are less likely to be repassivated; therefore, it leads to a deteriorated repassivation ability [118].

5. Conclusion

To conclude, we developed a novel nanostructured EHEA in this study, which exhibits excellent corrosion resistance and a superior self-repairing ability. Such high anti-corrosion performance is due to the combination of a compact surface high entropy oxide film with the nanostructure in the EHEA. To facilitate our understanding, the underlying corrosion mechanisms are depicted in Fig. 9. In principle, our EHEA is passivated due to the formation of a less defective or more compact amorphous oxide film on its surface, which leads to a rather low corrosion current density and large passivation region. Upon transpassivation, the FCC phase behaves as anodic sites and dissolves preferentially. Due to the small spacing (~100 nm) between these FCC phases, stable pitting is prohibited, leading to selective corrosion and a general corrosion like behavior. When the scanning potential is reversed, the passive oxide film re-forms on the nanostructured EHEA, showing a remarkable self-repairing ability. On the basis of our findings, we envision that, following the “eutectic nanostructure high entropy” design paradigm, one could design more corrosion-resistant EHEAs by further structural refining combined with the minor addition of proper elements, such as Al and Ti.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Figure Captions

Fig. 1. (a) The XRD pattern of the as-cast FeCrNiCoNb_{0.5} EHEA, (b) the typical microstructural features of the FeCrNiCoNb_{0.5} EHEA observed on the etched cross section, (c) the low magnification TEM image of the dual phase. The insets of (c) show the Fast Fourier Transformation (FFT) images of the FCC and Laves phase. (d) The HRTEM image of the inter-phase.

Fig. 2. (a) Potentiodynamic polarization curves of EHEA and 304 SS in 1 M NaCl solution. (b) A comparison of the corrosion current density (i_{corr}) and break down potential (E_b) between HEAs and other materials in 1 M NaCl solution at room temperature. (c and d) EIS of EHEA and 304 SS exposed to 1 M NaCl solution in the single-cylinder corrosion cell under open circuit potential condition: (c) Nyquist plots and (d) Bode plots. The inset of (c) shows the equivalent circuit. (e) Cyclic potentiodynamic polarization curves of EHEA and 304 SS in 1 M NaCl solution.

Fig. 3. Corrosion morphologies of EHEA (a)-(c) and 304 SS (d)-(f) at different selected time points on cyclic potentiodynamic polarization curves. (a)-(c) represents time points a-c in Fig. 2 (e) and (d)-(f) represents time points d-f in Fig. 2 (e). EDS spectra of zone 1 (g) and 2 (h).

Fig. 4. (a) The low magnification TEM image of the cross-sectional EHEA samples on which a passive film was formed, (b) the HRTEM image of the cross-section. The inset of (b) shows the Fast Fourier Transformation (FFT) images of the passive film. (c) STEM image of the cross-sectional EHEA samples and EDS line profiles along the yellow arrow in the STEM image. (d) The AFM image of the passivated EHEA surface. (e) Profiles along the white dash line in (d). (f) 3D topography image.

Fig. 5. (a) STEM image of the cross-sectional EHEA sample. EDS mapping distribution of (b) Nb, (c) Fe, (d) Cr, (e) Ni, (f) Co.

Fig. 6. (a) Mott-Schottky plots for the passive film formed on EHEA and 304 SS in 1 M NaCl solution at OCP for 3 h. (b) Flat band potential and donor densities of the passive films formed on EHEA and 304 SS.

Fig. 7. (a)-(c) AFM images of our EHEA at the time points a-c in Fig. 2 (e). (d)-(f) Profiles along the dash lines in (a)-(c). (g)-(i) 3D topography images corresponding to (a)-(c), respectively.

Fig. 8. (a) The typical microstructural features of the annealed EHEA alloy observed on the etched cross-section. (b) Cyclic potentiodynamic polarization curves of the as-cast and annealed EHEA in 1M NaCl solution. (c) Corrosion morphology of the annealed EHEA at the time point c on the cyclic potentiodynamic polarization curve.

Fig. 9. Schematic of the passivation, transpassivation and re-passivation mechanism on the EHEA surface during cyclic potentiodynamic polarization in 1M NaCl solution.

Tables

Table 1 Phase compositions of the FeCrNiCoNb_{0.5} EHEA (at.%).

Elements	Fe	Cr	Ni	Co	Nb
FCC	26.3	28.1	22.0	22.3	1.5
Laves	19.2	17.0	16.9	25.0	20.4

Table 2 Electrochemical parameters of EHEA and 304 SS in 1 M NaCl solution from potentiodynamic polarization curves.

Samples	E_{corr} (mV _{SCE})	I_{corr} (nA·cm ⁻²)	E_b (mV _{SCE})	Passive region (mV)
EHEA	-238 ± 12	24.29 ± 4.27	976 ± 23	1214 ± 33
304 SS	-196 ± 14	30.45 ± 3.48	346 ± 38	433 ± 45

Table 3 Summary of reported corrosion behaviour (derived from potentiodynamic polarization curves) of HEAs and conventionally alloys in 1 M NaCl solution. In this table corrosion parameters obtained from various papers are presented.

Materials	I_{corr} (nA·cm ⁻²)	E_{corr} (mV _{SCE})	E_b (mV _{SCE})	Passive region (mV)	Reference
FeCoNiCrNb _{0.5}	24	-238	976	1214	This study
FeCoNi	400	-493	-32	461	[77]
FeCoNiCr	280	-328	-34	294	[78]
FeCoNiNb	43000	-494	-235	259	[77]
CrFeMn _{0.5} Ni _{0.5}	450	-631	-222	409	[74]
FeCoNiNb _{0.5} Mo _{0.5}	33000	-455	295	750	[77]
Co _{1.5} CrFeNi _{1.5} TiMo _{0.1}	130	-622	973	1429	[32]
Co _{1.5} CrFeNi _{1.5} TiMo _{0.5}	200	-734	923	1383	[32]
Co _{1.5} CrFeNi _{1.5} TiMo _{0.8}	410	-792	941	1371	[32]
Co _{1.5} CrFeNi _{1.5} TiMo ₀	570	-684	97	557	[32]
Al _{0.3} CrFeMn _{0.5} Ni _{0.5}	690	-641	-391	250	[74]
Al _{0.5} CrFeMn _{0.5} Ni _{0.5}	1020	-741	-361	380	[74]
Cu _{0.5} NiAlCoCrFeSi	3160	-770	-490	280	[47]
CuYZrAlHf	146000	-1243	-949	294	[79]
CuYZrTiHf	159000	-1225	-945	280	[79]
CuYZrAlTi	235000	-1332	-850	482	[79]
304 SS ^a	30	-196	346	542	This study
202 SS ^a	24	-110	439	549	[80]
316L SS ^a	29	-90	606	696	[80]
Ion Nitriding 316L SS ^a	232	-654	-6	648	[81]
E309 DSS ^b	279	-243	431	674	[83]
E2209 DSS ^b	918	-266	492	758	[83]
UNS31803 DSS ^b	988	-229	924	1153	[83]
Carbon steel	41200	-651	- ^c	- ^c	[84]
AA2024-T3 ^d	86	-917	-704	213	[85]
AA2024-T3 ^d with LBP ^e	38	-907	-676	231	[86]
AA7075 ^d	1188	-896	-813	83	[87]
T240 ^d	70000	-712	-618	94	[88]
Ni-based alloy 22	40	-339	597	936	[89]
Ni _{50.8} Ti _{49.2}	2000	-380	358	738	[90]
Ti ₆₀ Cu ₁₄ Ni ₁₂ Sn ₄ Nb ₁₀	9500	-409	-182	227	[82]

^a Stainless steel

^b Duplex stainless steel

^c No passivation behavior

^d Aluminum alloys

^e Low plastic burnishing (LBP), which produces a surface layer with high residual compressive stress[86]

Table 4 Equivalent circuit elements values for EIS data corresponding to EHEA and 304 SS in 1 M NaCl solution.

Material	R_1 ($\Omega \text{ cm}^2$)	CPE_1		R_2 ($\Omega \text{ cm}^2$)	χ^2
		Y_0 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$)	n		
EHEA	4.06(2.1)	2.55×10^{-5} (1.2)	0.87	13.50×10^5 (15.4)	4.18×10^{-3}
304 SS	6.14(1.4)	2.97×10^{-5} (1.2)	0.94	7.88×10^5 (8.2)	3.47×10^{-3}

The error percentage of data fitting is indicated in parentheses.

Table 5 Corrosion parameters of EHEA and 304 SS obtained from cyclic polarization curves in 1 M NaCl solution

Samples	E'_{corr} (mV _{SCE})	E'_b (mV _{SCE})	E_{rp} (mV _{SCE})	$E'_b - E_{\text{rp}}$ (mV _{SCE})	E_{ptp} (mV _{SCE})
EHEA	-232 ± 12	979 ± 6	767 ± 38	212 ± 43	549 ± 21
304 SS	-185 ± 19	343 ± 20	-192 ± 11	536 ± 20	-197 ± 8