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Zhou, Q., Sheikh, S., Ou, P. et al (2019). Corrosion behavior of Hf<sub>0.5</sub> Nb<sub>0.5</sub> Ta<sub>0.5</sub> Ti<sub>1.5</sub> Zr refractory high-entropy in aqueous chloride solutions. *Electrochemistry Communications*, 98: 63-68.  
<http://dx.doi.org/10.1016/j.elecom.2018.11.009>

N.B. When citing this work, cite the original published paper.



# Corrosion behavior of $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$ refractory high-entropy in aqueous chloride solutions

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## ARTICLE INFO

### Keywords:

High-entropy alloys  
Refractory alloys  
Solid solution  
Corrosion  
Passivity

## ABSTRACT

The  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  refractory high-entropy alloy with excellent corrosion resistance in the 3.5 wt% NaCl solution is identified in this work. This refractory high-entropy alloy exhibits much better general corrosion resistance than that of the 316L stainless steel, due to its corrosion current density being about one fifth of that in the latter. Meanwhile, the pitting potential of  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  reaches an unusually high value of +8.36 V, much higher than that of reported high-entropy alloys. The superior passivity of  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  is accredited to the formation of a single-phase solid solution containing high amount of homogeneously distributed passivity-promoting elements, and also the existence of metallic Ta and  $\text{OH}^-$  species in the passive film, which contribute to the high immunity to passive film breakdown.

## 1. Introduction

Corrosion is one of the most common failure modes of metals, and the cost due to corrosion of metals has been over 3% of the world's gross domestic product annually in recent years [1]. To alleviate the formidable challenge, corrosion control is considered as one of the strategic areas for metals-based civilization [2]. Generally, some metals or alloys would show inherently low corrosion rates due to the formation of passive films. However, the localized pitting, which rapidly leads to the failure of metals, cannot be avoided once the passive film breaks down [3]. Accordingly, design and fabrication of new alloys with high passivity, have drawn much attention of materials scientists and engineers [4].

High-entropy alloys (HEAs), which are composed of at least four principal metallic elements, are newly emerging metallic materials [5]. The alloying concept that is brought by HEAs, opens up an enormously large and unexplored compositional space. HEAs, depending on compositions, have exhibited many attractive properties in terms of hardness, strength, wear resistance, and resistance to high-temperature softening [6,7]. Besides, some HEAs have shown excellent corrosion resistance due to the claimed good passivation characteristics [8–10]. It is therefore quite intriguing to further explore the potential of HEAs, as novel metallic materials that could have high passivity.

As reported, the superior passivity of HEAs can be understood and

explained based on their composition and structure. Usually, the HEAs with high corrosion resistance contains large amounts of passive elements such as group IVB elements (Ti, Zr, and Hf) and group VIB elements (Cr, Mo, and W), which facilitate the formation of stable barrier films [8–12]. Besides, the entropy stabilized single solid solution phase that is formed in HEAs can also contribute to preventing the pitting corrosion, which would preferably occur at the phase boundaries where the composition shows large variations [10]. However, to the best of our knowledge, pitting potential,  $E_{\text{pit}}$ , of known HEAs are no more than +3 V in the 3.5 wt% NaCl solution [9–18]. In other words, it remains to be a tremendous challenge to design novel alloys with high passivity. Here, we present a refractory HEA (RHEA) with surprisingly high  $E_{\text{pit}}$  in aqueous chloride solutions, which makes it a promising material to be used in extremely demanding and highly-sensitive service environments.

## 2. Experimental

The RHEA studied in this work,  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$ , was developed in our previous work [7]. It was prepared by arc melting high purity (> 99.9%) elemental materials on a water-cooled copper plate in the Ar atmosphere. The ingots were flipped and re-melted five times for improved homogeneity. The final ingot has the dimension of about 66 mm (length) × 28 mm (width) × 10 mm (thickness). After

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<https://doi.org/10.1016/j.elecom.2018.11.009>

Received 22 October 2018; Received in revised form 14 November 2018; Accepted 15 November 2018

Available online 16 November 2018

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solidification, the samples for experiments, with strictly the dimension of 10 mm × 10 mm × 1 mm, were prepared from the ingots by electrical discharge machining followed by grinding and polishing.

The microstructures and element distribution were investigated by back-scattering electron imaging (BSE), electron backscatter diffraction (EBSD) and energy dispersive spectroscopy (EDS) using a field-emission scanning electron microscope (NOVA NanoSEM 230, FEI). The crystal structure was examined by an X-Ray diffractometer (XRD, Bruker D8 Advance) using the Cu K-alpha radiation ( $\lambda = 1.5406 \text{ \AA}$ ), operating at 40 kV and 200 mA. Chemical compositions of the passive films formed on the HEA samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250XI, Thermo Fisher) using the Al K-alpha X-ray source (1486.6 eV).

The electrochemical measurements were performed using a Princeton PARSTAT4000A electrochemical workstation with a conventional three-electrode electrochemical cell, consisting of the HEA sample (with an exposed area of 1 cm<sup>2</sup>), Pt sheet saturated-calomel electrode (SCE) as the working electrode, counter electrode, and reference electrode. Before tests, RHEA samples were epoxy encapsulated, polished, degreased in alcohol, washed in distilled water and dried in air. All tests were carried out in the 3.5 wt% NaCl solution (pH = 7 ± 0.2, open to air) at ambient temperature (25 °C). The potentiodynamic-polarization tests were performed at a scan rate of 1 mV/s from an initial potential of −1.3 V till the current density reached a maximum of 1 mA/cm<sup>2</sup>. To confirm the data reproducibility, ten parallel Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA samples were measured and the standard deviation of the  $E_{\text{pit}}$  was calculated. The EIS tests were carried out at open circuit potential with a sinusoidal potential amplitude of 10 mV, running from 100 kHz to 10 mHz. For comparison, 316L stainless steels (SS) and pure Ti (> 99.9%) were also tested under the same condition.

### 3. Results and discussion

According to the BSE image, inverse pole figure (IPF) map and the XRD pattern as shown in Fig. 1, the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA forms a single-phase bcc solid solution with equiaxed grains. It is noted that here that the microstructure looks different to the microstructure that was reported for the same material before [7,19], mainly because of the different cooling rate that was used here and in previous work. The average grain size of the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA is ~160 μm. In addition, EDS mapping of constituent elements in Figs. 1c–g shows that each element distributes quite homogeneously. Here in Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr, a single bcc solid solution with homogeneously distributed passivating elements, is expected to possess a superior passive property.

As shown in the polarization curve in Fig. 2a, 316L SS exhibits a typical passivation behavior, and the extracted electrochemical parameters are quite analogous to previous studies [20]. For the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA, its corrosion current density ( $i_{\text{corr}}$ ) is about one fifth of that of 316L SS, indicating that the general corrosion resistance of this RHEA is much better than that of 316L SS. In addition, the excellent corrosion resistance of the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA could be confirmed by its  $i_{\text{corr}}$  being quite close to that of pure Ti (Fig. 2a).

More strikingly, a highly significant passivation behavior, as characterized by the extremely noble  $E_{\text{pit}}$  of +8.36 V (standard deviation = 0.11), can be observed. The protective film is formed almost spontaneously at the corrosion potential ( $E_{\text{corr}}$ ), based on the feature that the polarization curve changes directly into the passive region without a noticeable active to passive transition [11]. There exist two passive regions, with the first passive region (−0.1–1.47 V) showing a stable passive current density, whereas the second passive region (1.9–8.36 V) showing sporadic current fluctuations, due to the formation and re-passivation of metastable pits [21]. The current fluctuations occur sporadically and annihilate rapidly in this wide passive region,

indicating a strong film repairing ability [22,23]. In the second passive region, the passive current densities ( $i_{\text{pass}}$ ) of pure Ti increase gradually. By contrast, the  $i_{\text{pass}}$  of the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA is quite stable.

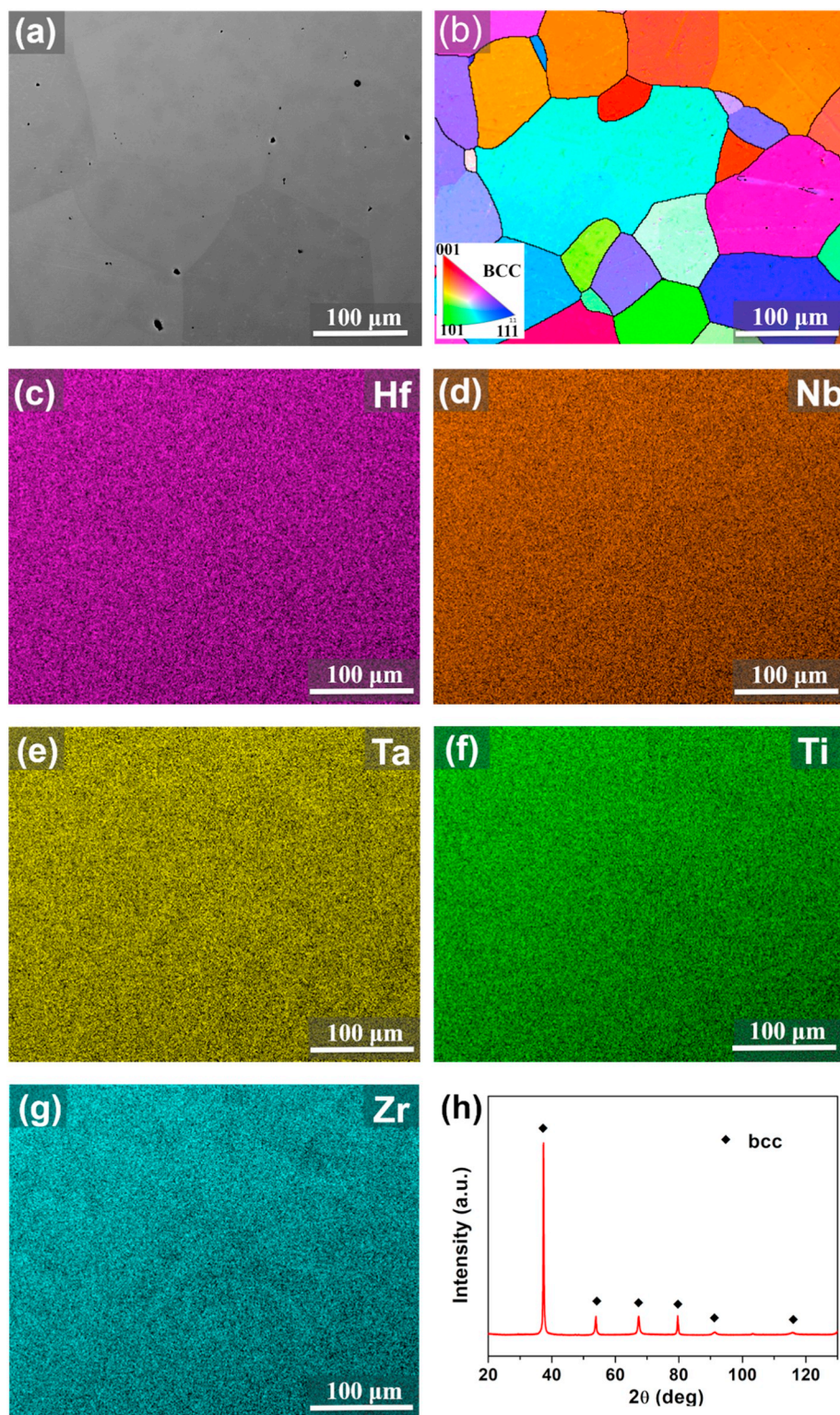
Fig. 2b–f show the Bode and Nyquist plots of the films formed on the RHEAs after passivation for 10 mins at the potentials within the passive region (specifically, 1.0 V, 1.9 V, and 5.0 V), and passivation for 3 mins at 8.5 V, respectively. Two electrical equivalent circuits in Fig. 2g ( $Q_{\text{pass}}$  and  $Q_{\text{pit}}$  are the constant phase element (CPE) for passive films without pits and containing pits/metastable pits, respectively;  $R_{\text{pass}}$  and  $R_{\text{pit}}$  are the polarization resistance depending on passive films without or with pits;  $R_{\text{ct}}$  is the charge-transfer resistance;  $R_s$  is the solution resistance) are used to fit the EIS spectra (Fig. 2g) [24,25]. As shown in the Bode plots (Fig. 2b), high and slanted impedance modulus values and the relatively stabilized phase angles (70–85°) at the medium-low frequencies for the samples passivated at the potentials within the passive region are observed, indicating a capacitive response which relates to the presence of the barrier passive films [26,27]. All the Nyquist plots (Fig. 2c–f) are characterized by an unfinished semi-circle, a feature which is potential dependent [27]. Meanwhile the values of impedance ( $|Z|$ ) increase with the increase of passivation potentials (Fig. 2b), due to the increase of passive film thickness ( $\delta$ , which could be compared by  $1/Y_0$ , here  $Y_0$  is the proportionality factor for CPE impedance) and in the order of ( $Y_{0-1.0\text{V}} > Y_{0-1.9\text{V}} > Y_{0-5.0\text{V}}$ ) [11]. In addition,  $R_{\text{pass}}$  or  $R_{\text{pit}}$  of the samples passivated at the potentials in the passive region are tremendously high ( $R_{\text{pass-1.0V}} = 2.78 \times 10^{15}$ ,  $R_{\text{pass-1.9V}} = 6.64 \times 10^{14}$ ,  $R_{\text{pit-5.0V}} = 6.13 \times 10^{14} \Omega\text{cm}^2$ , respectively), confirming that the formed passive films can act as semi-conductive barriers to anti-corrosion. By contrast, the sample passivated at 8.5 V shows a feature of passive breakdown, according to the characteristics of non-existent capacitive-like behavior (Fig. 2b), and the low  $R_{\text{pit}}$  value ( $R_{\text{pit-8.5V}} = 2.97 \times 10^3 \Omega\text{cm}^2$ , shown in Fig. 2f).

To thoroughly understand these passivation behaviors, the passive films formed on the RHEAs were analyzed by XPS (Fig. 3). When the polarization tests run to the critical potentials within the passive region, the passive film is composed of a mixture of TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and Ta<sub>2</sub>O<sub>5</sub> (Fig. 3b–f) [28,29]. All these species with stable chemical states have been demonstrated to benefit the formation of continuous, stable and protective passive films [8,28–30]. Meanwhile, OH<sup>−</sup> species and metallic state Ta are also observed (Fig. 3a, d). The OH<sup>−</sup> species, which may come from the hydrated metal oxides or adsorbed H<sub>2</sub>O, can repair the passive film integrity and increase the resistance to the attack from chloride ions [28,31,32]. The metallic state Ta, a unique feature for the protective passive film formed on Ta alloys [8,33], has also been found on the surface of  $\beta$  type Ti–Ta–Hf–Zr alloys after polarization within the passive region [34]. By contrast, there exist no OH<sup>−</sup> species and metallic Ta on the surface of samples after polarization to the transpassive region (8.5 V) (Fig. 3a). Instead, besides the highly charged and stable oxides species (TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>), suboxide species such as Zr<sub>2</sub>O<sub>3</sub>, NbO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, Hf<sub>2</sub>O<sub>3</sub>, TaO<sub>2</sub> are detected in the destructed film (Fig. 3b–f) [8]. Ti<sub>2</sub>O<sub>3</sub> is regarded as the inducement for the metastable pits [30]. Besides, suboxides such as Zr<sub>2</sub>O<sub>3</sub>, Hf<sub>2</sub>O<sub>3</sub>, NbO<sub>2</sub>, and TaO<sub>2</sub> seen in the passive film are also regarded as un-protective oxides [8].

It seems that the existence of metallic Ta and OH<sup>−</sup> species in the passive film could be responsible for the superior passivity of the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA. Furthermore, another factor should also be considered: the alloying concept of HEAs ensures that the high content of passivity-promoting elements is homogeneously distributed in the single-phase solid solution. Therefore, the compositional limit of added elements can be relaxed, so more passivity-promoting elements than in conventional alloys can be added. Besides, the preferential corrosion occurred in the phase boundaries or inhomogeneous compositions could be avoided, thanks to the formation of a homogeneous single-phase solid solution [10].

In summary, it can be concluded that a superior corrosion resistance is achieved in the Hf<sub>0.5</sub>Nb<sub>0.5</sub>Ta<sub>0.5</sub>Ti<sub>1.5</sub>Zr RHEA, and is accredited to





**Fig. 1.** a: BSE image, b: IPF map, c–g: EDS mapping and h: XRD pattern of the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA.

both the formation of a single-phase solid solution containing high amount of homogenously distributed passivity-promoting elements, and the high stability of the formed passive film.  $E_{\text{pit}}$  of the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA reaches an unusually noble value of +8.36 V. Nowadays, enormous efforts have been motivated to design new alloys to improve the resistance to localized corrosion. A detailed comparison of the corrosion behavior between the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA, and conventional passive alloys (Ni-, Ti-,

Cu-, Al-based alloys and stainless steels) and other reported HEAs in the 3.5 wt% NaCl solution is plotted in Fig. 4 [9–18,20,35,36]. As shown in Fig. 4, some HEAs already exhibit higher  $E_{\text{pit}}$  than that of conventional passive alloys. Particularly, the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA that is studied here, exhibits the highest  $E_{\text{pit}}$  among all reported HEAs, showcasing the tremendous possibility of RHEAs for future applications, such as seawater desalination, naval armament, and chemical vessels.

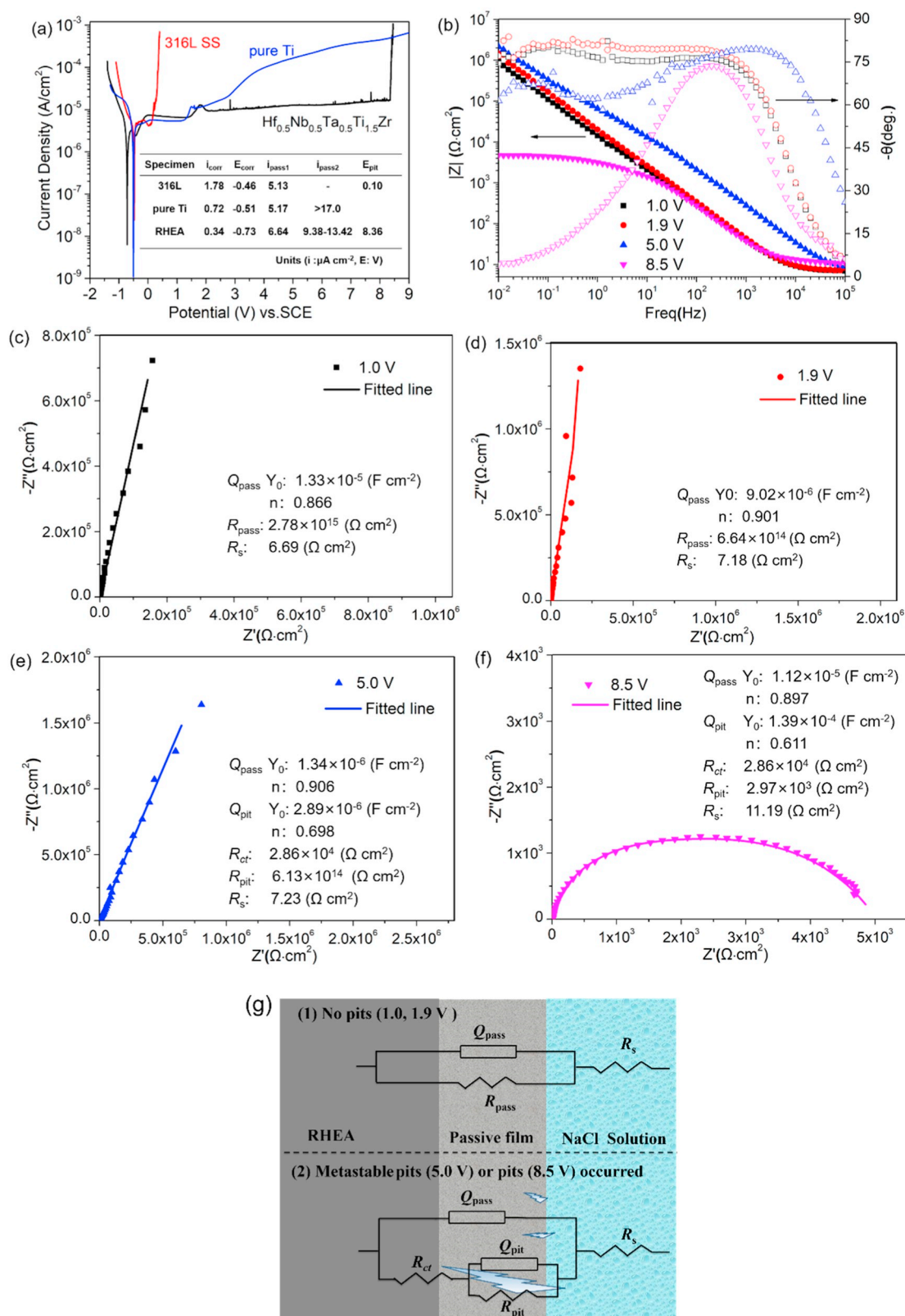


Fig. 2. a: Polarization curves of the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA, 316L SS and pure Ti in the 3.5 wt% NaCl solution, b–f: Nyquist and Bode plots of the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA in the 3.5 wt% NaCl solution, g: Equivalent electrical circuit for fitting the EIS experimental data.

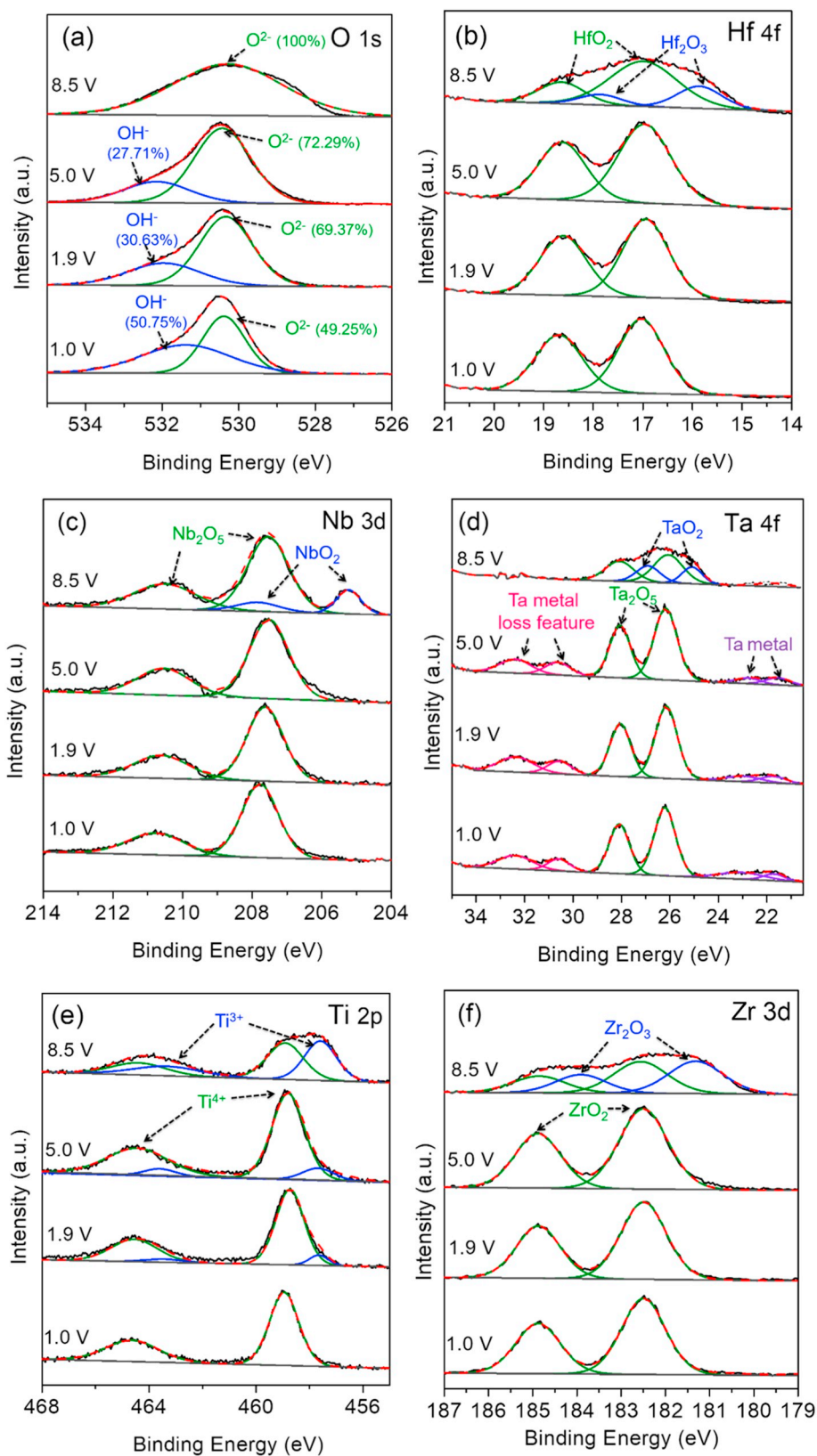


Fig. 3. XPS spectra made at the outer surface of samples after polarization ran to the chosen potentials.



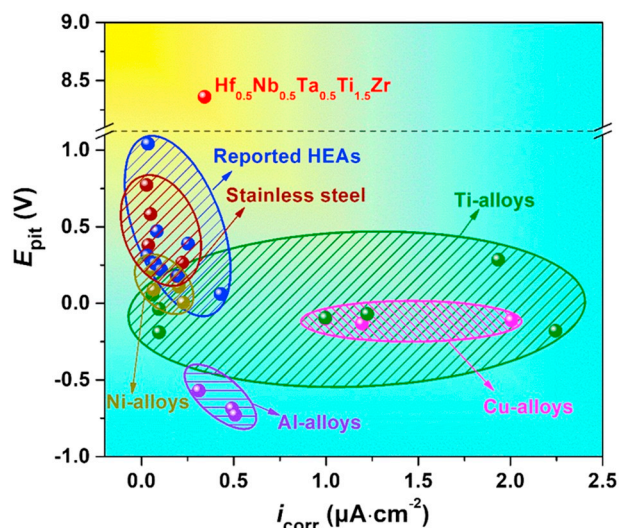


Fig. 4. Comparison of  $E_{\text{pit}}$  and  $i_{\text{corr}}$  for the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA, previously reported HEAs, and some conventional passive alloys in the 3.5 wt% NaCl solution.

#### 4. Conclusion

The corrosion resistance of the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA in the 3.5 wt% NaCl solution is investigated in this work. This RHEA exhibits much better general corrosion resistance than that of 316L SS, due to its much lower corrosion current density. Meanwhile, an unusually noble  $E_{\text{pit}}$  of +8.36 V for the  $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$  RHEA is revealed. The superior passivity is mainly attributed to the formation of a single-phase solid solution containing high amount of homogeneously distributed passivity-promoting elements (Hf, Nb, Ta, Ti and Zr), and the existence of metallic Ta and  $\text{OH}^-$  species in the passive film. The work presented here exemplifies that the alloying strategy of HEAs could be an important future research direction, to meet the global challenge of corrosion control.

#### Acknowledgements

This work is supported by the National Natural Science Foundation of China (51504104), Natural Science Foundation of Jiangxi Province, China (20161BAB206141). SS and SG are grateful for the financial support from Areas of Advance Materials Science from Chalmers University of Technology.

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