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STRUCTURE, PHASE TRANSFORMATIONS,  
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## Electrochemical Properties of TiAl-Based Alloys

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**Abstract**—TiAl alloys represent a promising potential for use in many fields including automotive, aerospace and marine industries. Therefore, it can be considered important to investigate the ability of these alloys to withstand such harsh environments. To this intended, the following study attempted to determine the electrochemical properties of Ti–48Al–2Mo–2(Cr,Mn) (at %) alloys in 3.5 wt % NaCl solution. The results of potentiodynamic polarization experiment revealed that Mo addition can enhance the corrosion resistance of the alloys, especially the Ti–48Al–2Cr alloy. Ti48Al–2Cr–2Mo was found to have the lowest corrosion rate value of 0.1153 mm/year, whereas Ti48Al–2Mn was found to have the highest corrosion rate value of 0.3952 mm/yr. The polarization resistance ( $R_p$ ) of the alloys changes from 1.33 to 5.54 k $\Omega$  cm<sup>2</sup> depending on alloyed compositions. The electrochemical impedance spectroscopy (EIS) results confirmed that the corrosion behavior can be tailored through Mo addition. Accordingly, the best corrosion resistance belongs to the Ti48Al–2Cr–2Mo alloy, which presents the highest impedance value of  $4.98 \times 10^3 \Omega$ . The surface morphologies of corroded alloys exhibited the pitting corrosion characteristics after the polarization experiments in 3.5 wt % NaCl solution. The number density of corrosion pits was significantly higher on the surfaces of the Ti48Al–2Mn and Ti48Al–2Mn–2Mo alloys. The enhanced corrosion resistance of Ti48Al–2Cr–2Mo alloy to NaCl solution is believed to be associated with the coupled positive effect of Cr and Mo in forming a surface film with a good protective ability. In addition, Ti48Al–2Cr–2Mo exhibited high resistance to NaCl solution at a level, which can be considered an optimum material for fabricating parts that serve in the marine environment.

**Keywords:** TiAl, NaCl solution, electrochemical behavior, alloying elements

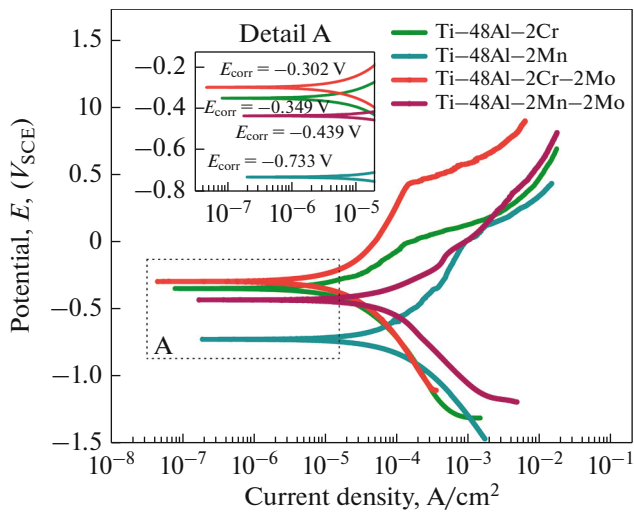
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### INTRODUCTION

In the past few decades, TiAl alloys have gathered significant interest from researchers who are committed to materials research and development in the academic community and industrial sectors because of their remarkable properties like low density (3.9–4.2 g cm<sup>-3</sup>), high melting point, high specific yield strength, good creep properties as well as adequate oxidation and corrosion resistance [1–5]. The combination of all these unique properties makes TiAl alloys have a wide broad of engineering applications in the field of aerospace and automotive, especially they are considered suitable candidates for turbine blades in aero-gas turbines and turbocharger rotors in automotive engines [6]. One of the main qualities expected from materials driven by the demand to meet the current requirements in such application areas is resistance against chemically challenging mediums such as corrosive salt and acid solutions. Due to the growing demand for the design of TiAl alloys with excellent properties, many studies have been led to enhance the properties of these alloys, most of which are related to their mechanical [7–9] and oxidation [10–12] responses.

However, according to the best of our knowledge, there are limited works available addressing the electrochemical behavior of TiAl alloys in various corrosive solutions, which puts forward more attention to be paid to the electrochemical properties of these alloys.

TiAl alloy designed by adding various alloying elements can be regarded as an effective approach to enhance the corrosion behavior of these alloys. Mo addition has been stated to play a leading role in enhancing the passivity and corrosion performance of Ti alloys [13, 14]. Mn and Cr additions were selected as alloying elements in this work because they have lower cost and higher availability as compared to other elements such as scarce Ta and Nb. However, Pardo et al. [15] have found that the addition of Mn into the austenitic stainless steel increases the corrosion rate in chloride-containing solution. Whereas, Cr addition has been reported to be beneficial for improved corrosion performance in acidic solutions [16]. Therefore, it is important to determine the effects of Mo, Mn and Cr alloying elements on the corrosion behavior of TiAl alloy in NaCl corrosive solution. To this end, the designed Ti–48Al–2Mo–2(Cr, Mn) alloy is believed



**Fig. 1.** The potentiodynamic polarization curves of TiAl alloys in 3.5 wt % NaCl solution.

to be a potential candidate to attain the intended perspective. This work addressed the role of Cr, Mn and Mo alloying elements on the electrochemical corrosion properties of TiAl alloys in 3.5 wt % NaCl solution.

## EXPERIMENTAL

Ti-48Al-2Mo-2(Cr,Mn) (at %) alloys investigated in this study were obtained through powder metallurgy merged with an electric current assisted sintering process (ECAS), the production details were provided in our previous study [4]. The electrochemical measurements were conducted on an electrochemical workstation (PCI4/750/ZRA, Gamry Instrument) with a standard three-electrode cell system. A saturated calomel electrode (SCE) served as a reference electrode (RE) and a graphite rod was the counter electrode (CE). The TiAl sample was adapted as a working electrode (WE) with a surface area of 0.785 cm<sup>2</sup>, and the electrolyte was 3.5 wt % NaCl solution. All experiments were performed at room temperature. Potentiodynamic polarization curves were measured at a scan rate of 1 mV/s and the potential scanning range was from -1.5 to 0.9 V. After electrochemical measurements, tafel extrapolation technique

on anodic and cathodic branches was applied to acquire the corrosion potential ( $E_{\text{corr}}$ ) and the corrosion current density ( $I_{\text{corr}}$ ). Electrochemical impedance spectroscopy (EIS) analyses were conducted at Open circuit potential (OCP) in the frequency ranging from 10<sup>-1</sup> to 10<sup>5</sup> Hz. The surface morphology of corroded alloys was examined using a scanning electron microscope (SEM, JEOL JSM-6060, LV).

## RESULTS AND DISCUSSION

The potentiodynamic polarization curves for all of the four TiAl alloys exposed in 3.5 wt % NaCl solution are illustrated in Fig. 1. These curves are quite beneficial for revealing some electrochemical parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ), and Tafel constants (anodic polarisation ( $\beta_a$ ) and cathodic polarisation ( $\beta_c$ )). The mentioned parameters in Table 1 are derived from the polarization curves by analyzing the linear part of the anodic and cathodic branches corresponding to the investigated alloys. As can be seen in Table 1, some shifts in the  $E_{\text{corr}}$  values and a notable difference in the  $I_{\text{corr}}$  values of the alloys are evident, which allows us to say that the corrosion resistance of TiAl alloys is affected by the addition of alloying elements. According to Table 1,  $E_{\text{corr}}$  values of the alloys are in the range from -0.733 to -0.302 V, while their  $I_{\text{corr}}$  values are in the range of  $4.56 \times 10^{-5}$  to  $1.39 \times 10^{-5}$  A/cm<sup>2</sup>. For the sake of comparison, the  $E_{\text{corr}}$  of the TiAl-2Cr has shifted in a nobler direction compared to the TiAl-2Mn, and also the  $I_{\text{corr}}$  value is decreased by approximately 2.6 times for TiAl-2Cr, which implies that the addition of Cr into TiAl alloy improves the corrosion behavior more effectively. The noticeable effect of Cr element on the corrosion performance may correspond to its passivation behavior, which effect is consistent with increased  $E_{\text{corr}}$  and decreased  $I_{\text{corr}}$  values. It has been stated that the descending sequence of passivation ability is Cr, Ni, Co, Fe, Mn and Cu in the multicomponent alloys [17], providing an indication that the ability of Cr to form a protective film on the surface plays a crucial role in determining the corrosion tendency. Regarding the role of Mn addition on corrosion resistance of TiAl alloy, the effect of Mn on the corrosion property of Ti-24Nb-4Zr-xMn ( $x = 0, 1, 3, 5$  wt %) alloy in Ringer's solution has been

**Table 1.** Electrochemical parameters of TiAl alloys exposed in 3.5 wt % NaCl solution

Alloys, at %	$E_{\text{corr}}$ , V	$I_{\text{corr}}$ , A/cm <sup>2</sup>	$\beta_a$ , V/dec	$\beta_c$ , V/dec	$R_p$ , k $\Omega$ cm <sup>2</sup>
Ti-48Al-2Cr	-0.349	$1.74 \times 10^{-5}$	0.288	-0.375	4.06
Ti-48Al-2Mn	-0.733	$4.56 \times 10^{-5}$	0.329	-0.242	1.33
Ti-48Al-2Cr-2Mo	-0.302	$1.39 \times 10^{-5}$	0.344	-0.367	5.54
Ti-48Al-2Mn-2Mo	-0.427	$4.07 \times 10^{-5}$	0.255	-0.278	1.42

explored by Wu et al. [18]. Their electrochemical measurements revealed that the corrosion resistance is enhanced with the increase of Mn content. Though the enhanced corrosion resistance was attained by the addition of Mn, there was a slight improvement in the corrosion resistance, as reported in [18], for the alloy with 3 wt % Mn in comparison with the alloy without Mn. However, the prevailing tendency of Cr element in decreasing corrosion rate overshadowed the effect of Mn element on the alloys examined in this work when the  $E_{\text{corr}}$  and  $I_{\text{corr}}$  values corresponding to the alloys are co-considered. As for the TiAl alloys with the addition of Mo, the Mo element seems to play a beneficial role in increasing the corrosion resistance of the alloys, based on the results presented in Table 1. It can be noticed that Mo addition exerts significant effects on the  $E_{\text{corr}}$  and  $I_{\text{corr}}$  of the alloys compared to those found for the alloys without Mo addition. Moreover, among the four alloys examined, TiAl–Cr–Mo alloy shows the best corrosion behavior with the lowest value of  $I_{\text{corr}}$  and the highest value of  $E_{\text{corr}}$  under the experimental conditions used in this work. A similar explanation may also hold good for TiAl–Mn–Mo alloy, as an improvement in corrosion resistance of TiAls is noted with an increase in  $E_{\text{corr}}$  and a decrease in  $I_{\text{corr}}$ . The results presented above corresponding to the effect of Mo addition are consistent with the statement that Mo content increases the corrosion resistance of Ti alloys with various compositions [14, 19], in which corrosion results of the alloys characterized by electrochemical measurements confirmed that Mo lowers the corrosion rate of the Ti alloys to a level comparable to that of pure Ti.

In order to present the readers an insight into the general corrosion tendency of TiAl alloys investigated in this work, a comparison including the  $I_{\text{corr}}$  and  $E_{\text{corr}}$  values of Ti alloys with various compositions [20–24] was performed in Fig. 2. From the comparison in Fig. 2, it can be concluded that the mentioned data of the studied alloys lie close to those reported in the literature, except for [20, 21].

Moreover, polarization resistance ( $R_p$ ) is considered a considerable parameter in characterizing the corrosion resistance of the materials.  $R_p$  can be calculated using the following equation [25]:

$$R_p = \frac{\beta_a \beta_c}{2.303 i_{\text{corr}} (\beta_a + \beta_c)}. \quad (1)$$

Table 1 presents the obtained  $R_p$  values corresponding to the TiAl alloys, and their  $R_p$  values change from 1.33 to 5.54  $k\Omega \text{ cm}^2$  depending on the designed compositions.  $R_p$  is inversely proportional to the corrosion rate, that is to say, the greater  $R_p$  value is, the slower the corrosion rate is. With alloying elements variation, the corrosion resistance can be ranked as: TiAl–Mn < TiAl–Mn–Mo < TiAl–Cr < TiAl–Cr–Mo under the selected experimental conditions, which

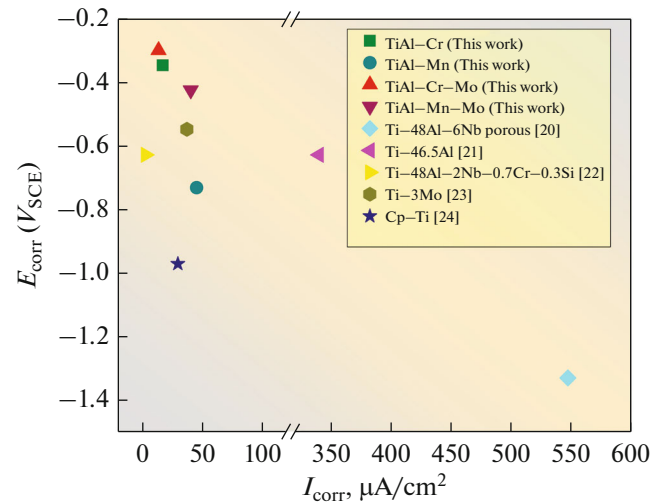


Fig. 2. Comparison of  $I_{\text{corr}}$  and  $E_{\text{corr}}$  of investigated alloys and Ti alloys with various compositions in 3.5 wt % NaCl solution.

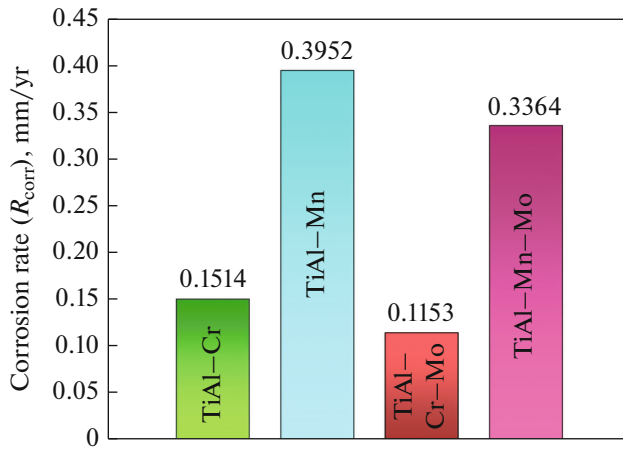
is in line with the polarization curves from Fig. 1, where the best corrosion behavior is found for TiAl–Cr–Mo alloy. However, the electrochemical parameters derived from the polarization curves may not always be satisfactory to determine the corrosion properties of materials. In this regard, the function of atomic-fraction-weighted values of atomic weight, the density of the alloy and ion valence also have to be taken into account to reveal the corrosion rate ( $R_{\text{corr}}$ ). Thus, the following equation can be considered to calculate the general corrosion rate ( $R_{\text{corr}}$ ) of the alloys [26]:

$$R_{\text{corr}} = 0.00327 (I_{\text{corr}} \text{EW}) / D, \quad (2)$$

where  $R_{\text{corr}}$  is the corrosion rate (mm/year),  $I_{\text{corr}}$  is the corrosion current density ( $\mu\text{A}/\text{cm}^2$ ), EW is the equivalent weight and  $D$  is the density ( $\text{g}/\text{cm}^3$ ). EW can be estimated as follows:

$$\text{EW} = \left( \sum \frac{f_i n_i}{A_i} \right)^{-1}, \quad (3)$$

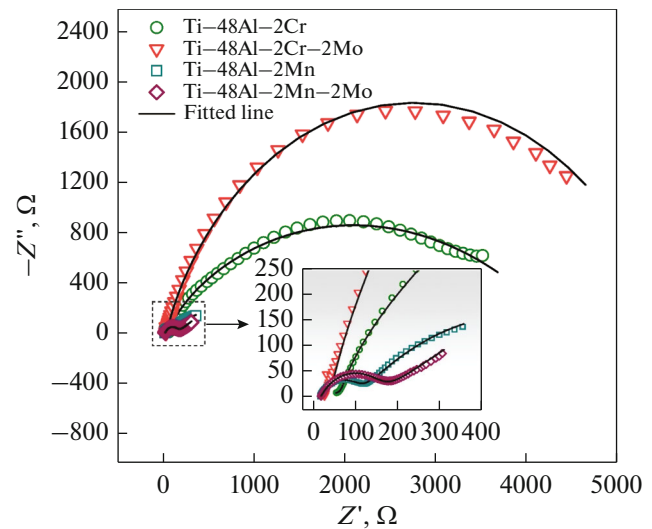
where  $f_i$ ,  $n_i$  and  $A_i$  represent the mass fraction, electrons exchanged, and atomic weight, respectively, of the  $i$ th alloying elements. The obtained  $R_{\text{corr}}$  values for the TiAl alloys are put forward in Fig. 3, in which the lowest one is found for the TiAl–Cr–Mo (0.1153 mm/yr) and the highest one is found for the TiAl–Mn (0.3952 mm/yr). The TiAl alloy having Cr and Mo additions has the highest corrosion resistance due to the fact that a low value of  $R_{\text{corr}}$  is associated with high corrosion resistance. In the case of TiAl–Cr alloy, the removal of Mo element from TiAl–Cr–Mo alloy brought up the value of  $R_{\text{corr}}$  to 0.1514 mm/yr, which has the second-lowest value. Compared to TiAl–Cr, the corrosion resistance of TiAl–Cr–Mo increased by 24%. However, when Mo is absent from



**Fig. 3.**  $R_{\text{corr}}$  values of TiAl alloys exposed in 3.5 wt % NaCl solution.

the TiAl-Mn alloy, the alloy experiences the highest corrosion rate, and its value of  $R_{\text{corr}}$  is noticed to be much higher, corresponding to 0.3952 mm/year, which represents around 15% deterioration in corrosion resistance compared to that observed for TiAl-Mn-Mo. One can be seen that Mo addition yields a positive effect on the corrosion behavior of both alloys, i.e. TiAl-Cr and TiAl-Mn, however, it should be noted that Mo reveals a stronger influence on the former. Anti-corrosion ability of Mo addition was attributed to the presence of  $\text{Mo}^{6+}$  ions in the passive film constituted on the surface, making it more stable against degradation induced by the invasion of aggressive  $\text{Cl}^-$  ions. Furthermore, the addition of Mo was reported to be responsible for the improvement of the repassivation behavior of the alloy [15]. In line with the reported findings, the better corrosion resistance caused by the addition of Mo is likely to be as a result of the passive film formed on the TiAl alloys being more stable to  $\text{Cl}^-$  ions attacks. At the same time, the microstructure-property relations of the alloys can present meaningful results regarding their corrosion behaviors. According to [4], all of the alloys were made up of TiAl and  $\text{Ti}_3\text{Al}$  phases, namely, the alloying process did not affect the phase constituents of TiAls. Besides that, as dissimilar to those of other TiAls, TiAl phase in the microstructures of both Mo-containing alloys was Mo-rich. Consequently, this may explain why Mo-containing TiAl alloys have enhanced corrosion resistance.

The electrochemical impedance spectroscopy (EIS) studies were conducted to shed more light on the electrochemical properties of the alloys and to further understand the electrochemical reactions that emerged at the electrode/electrolyte interface in 3.5 wt % NaCl solution. Accordingly, the measured Nyquist data for the TiAl alloys are plotted in Fig. 4 and the corresponding Bode plots are presented in Fig. 5. At first sight at the Nyquist spectra shown in



**Fig. 4.** Nyquist plots and fitted lines of TiAl alloys in 3.5% NaCl solution. The insert indicates the details of the Nyquist plots.

Fig. 4, the curves are observed to consist of unfinished semi-arcs with their centers depressed below the  $x$ -axis. This observation is typically featured in the non-perfect capacitive behavior of the surface [27]. The curves of TiAl-Cr and TiAl-Cr-Mo alloys appear to have a similar shape. To be more specific, the Nyquist spectra of these alloys include one capacitive loop from high to low frequency, each of which has a different semi-arc diameter. The observed one capacitive loop in Fig. 4 corresponding to TiAl-Cr and TiAl-Cr-Mo alloys indicates the presence of one time constant. However, clearly from Fig. 4, two capacitive loops at high and low frequency ranges can be observed for the Nyquist spectra of TiAl-Mn and TiAl-Mn-Mo alloys, signifying the existence of two capacitive time constants. It can be inferred that a different corrosion behavior is valid for these alloys compared to TiAl-Cr and TiAl-Cr-Mo alloys, in that the corresponding Nyquist curves include two capacitive loops with reduced diameters. The appearance of two capacitive loops has been reported to be associated with the severe degradation of corrosion resistance, ascribed to the formation of a porous surface film [28]. The diameters of the semi-arcs for TiAl alloys in Nyquist plots evidently differ. The largest semi-arc diameter is observed for TiAl-Cr-Mo alloy. Further, a decrease in the diameter of the semi-arc is noted for the TiAl-Cr alloy due to the removal of Mo element from TiAl. Dissimilar to what is observed on the TiAl-Cr and TiAl-Cr-Mo alloys, the remaining alloys, i.e., TiAl-Mn and TiAl-Mn-Mo, on the other hand, appear to present similar features with reduced diameters of the semi-arcs, with TiAl-Mn-Mo being slightly larger than TiAl-Mn in terms of semi-arc diameter. Another point worth noting is the coupled

effect of Cr and Mo is much more prominent than that of Mn and Mo, as evidenced in Fig. 4 by the EIS results. Such a result may be an indication that both alloys are governed by different corrosion mechanisms. This is remarkable in terms of the corrosion performances of alloys. The diameter of the semi-arc in Nyquist plots provides a useful indication for the fact about alloying element-induced improvement of the corrosion resistance of TiAl alloys. That is to say, the larger the diameter of the semi-arc is, the higher the corrosion resistance of the alloys [29], further indicating that the occurrence of a low corrosion rate is represented by greater impedance values at lower frequency in the Bode plot. In view of this consideration, a comparison of semi-arc sizes of four TiAl alloys points out that TiAl–Cr–Mo alloy owns the largest semi-arc size, representing the best corrosion performance. This evidence affirms that the presence of Mo significantly increases the corrosion resistance of TiAl–Cr alloy in NaCl solution, as can be seen in Fig. 4. Moreover, enhanced resistance signifies that chemical reactions will be more difficult to happen in the surface film of the TiAl–Cr–Mo alloy during the corrosion process. When this comparison is made with those observed in Mn-containing alloys, it is clearly visible that the alloys have a much smaller semi-arc size, which characterizes these alloys as more susceptible to corrosion under the same experimental conditions. A lower corrosion performance for the case of TiAl–Mn and TiAl–Mn–Mo alloys is most likely a manifestation of the weakened protective ability of surface film. The Nyquist plot evidently confirms that alloying elements can play a role as a determining factor in the corrosion performance of TiAl alloys. Additionally, it is worth emphasizing that the observed trend is in line with the corrosion results inferred from the polarization curves presented in Fig. 1.

Bode spectra with Bode-phase and Bode-magnitude plots for TiAl alloys are presented in Fig. 5. The phase angles of the alloys drop to near zero degrees at high frequencies, indicating that the impedance is governed by electrolyte resistance in this frequency range. In the medium-frequency region, the phase angles corresponding to the alloys rise and attain their own maximum values. Among the alloys investigated, TiAl–Cr–Mo alloy possesses the highest phase angle corresponding to about  $65^\circ$ , while the TiAl–Cr alloy takes second place with a phase angle of about  $45^\circ$ . It can be observed that the Bode-phase and Bode-magnitude plots are similar for TiAl–Mn and TiAl–Mn–Mo alloys. The smallest phase angle is observed for these two alloys. Furthermore, unlike those of TiAl–Cr and TiAl–Cr–Mo alloys, two peaks can be noticed in the Bode phase plots of TiAl–Mn and TiAl–Mn–Mo alloys, which attribute to the appearance of two-time constants. The effects of alloying elements on the Bode plots can determine the corrosion resistance of

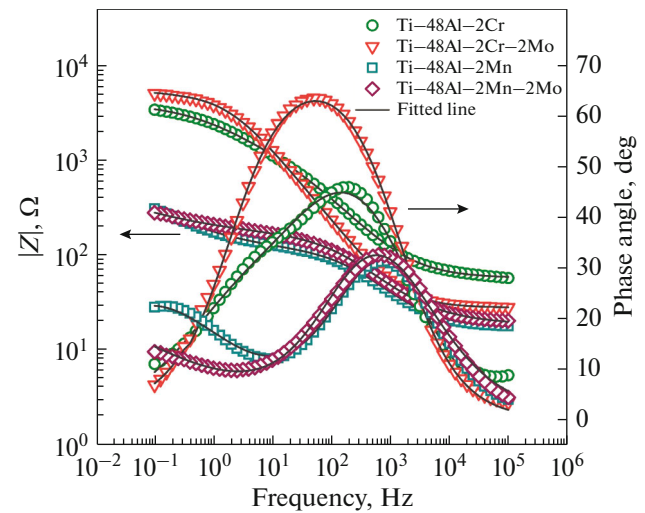
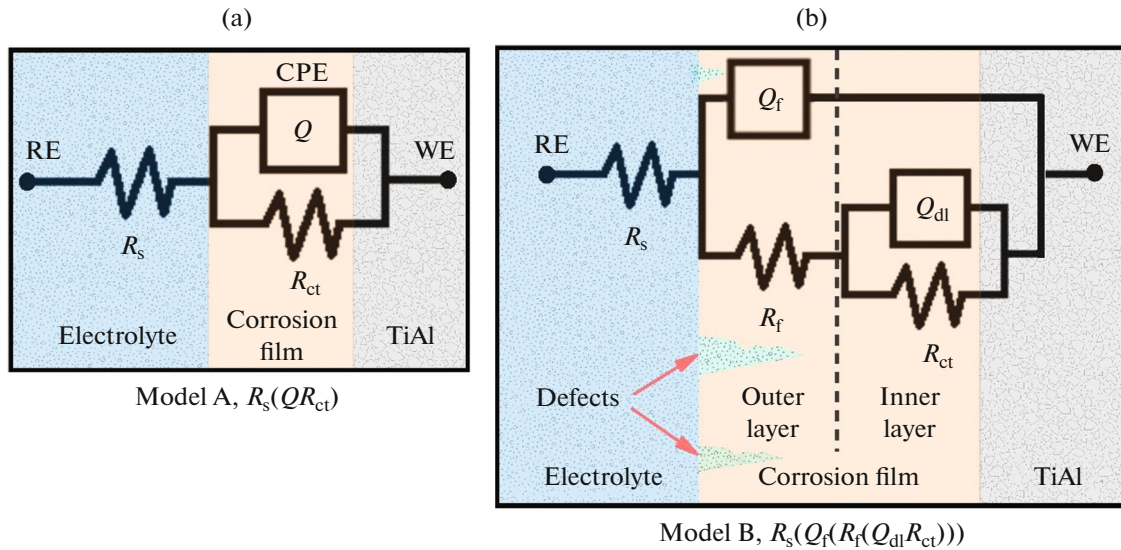


Fig. 5. Bode plots and fitted lines of TiAl alloys in 3.5% NaCl solution.

the alloys. To be specific: the higher values of impedance and maximum phase angle correspond to better corrosion resistance. The impedance value ( $|Z|$ ) at a fixed frequency of 0.1 Hz in the Bode-magnitude plots is an effective tool for the evaluation of the corrosion performance of the alloy [30]. As shown in Fig. 5, the impedance values at 0.1 Hz for the TiAl alloys are in descending order as follows: TiAl–Cr–Mo  $>$  TiAl–Cr  $>$  TiAl–Mn–Mo  $\cong$  TiAl–Mn. Accordingly, the best corrosion resistance belongs to the TiAl–Cr–Mo alloy, which presents the highest impedance value of  $4.98 \times 10^3 \Omega$ .

The EIS results are fitted using the equivalent electrical circuit (EEC) models to further analysis of the Bode spectra. Two different EEC models are applied to fit the EIS results of the TiAl alloys, as shown in Figs. 6a, 6b. Model A comprises the  $R_s$  connected in series with a parallel combination of a constant phase element (CPE,  $Q$ ) and an  $R_{ct}$ , where  $R_s$  is the electrolyte resistance, CPE is associated with the capacitance of the surface film and  $R_{ct}$  is the charge transfer resistance. Model B shows that the  $R_s$  is connected in series with four elements, as can be monitored in Fig. 6b. This adopted EEC model consists of two-time constants; the first of which corresponds to the high-frequency time constant ( $Q_f$ ) and is associated with the defective corrosion film formed on the alloy and the latter of which is the low-frequency time constant ( $Q_{dl}$ ) representing the charge transfer process that occurred on the surface of alloy [31]. In this model, the paralleled  $Q_f$ – $R_f$  refer to the surface film capacitance and surface film resistance, respectively. The paralleled  $Q_{dl}$ – $R_{ct}$ , which is connected in series with  $R_f$ , corresponds to the capacitance of the double layer and charge transfer resistance, respectively. The CPE is introduced instead of the ideal capacitance element



**Fig. 6.** The equivalent electrical circuits for fitting the EIS data of the TiAl alloys, (a) Ti48Al–2Cr and Ti48Al–2Cr–2Mo, (b) Ti48Al–2Mn and Ti48Al–2Mn–2Mo.

due to the inhomogeneous surfaces and adsorption effects. The CPE impedance ( $Z_{CPE}$ ) can be described as follows [32]:

$$Z_{CPE} = \frac{1}{Y_0} (j\omega)^{-n}, \quad (4)$$

where  $Y_0$  is the admittance magnitude of the CPE,  $j$  is the imaginary unit, and  $\omega$  is the angular frequency. The value of  $n$  describes the deviation from the ideal capacitive behavior, which changes from 0 to 1. When the  $n$  is 0, the CPE denotes an ideal resistor; when the  $n$  is 1, it describes an ideal capacitor; when the  $n$  is 0.5, it behaves as a Warburg impedance [29].

Table 2 presents the fitting parameter values of the electrochemical impedance data. From Table 2, the chi-square ( $\lambda^2$ ) values are found to be lying in the range of  $10^{-3}$  to  $10^{-4}$ , indicating that it can be considered to be good fitting quality. The total resistance in the proposed circuits determines the corrosion perfor-

mance of the alloys. The total resistance of TiAl–Cr and TiAl–Cr–Mo alloys corresponds to  $R_{ct}$  in model A, while that of TiAl–Mn and TiAl–Mn–Mo alloys equals to  $R_f + R_{ct}$  in model B. A higher resistance reflects a lower electrochemical reaction rate, which is responsible for enhanced corrosion resistance. It can be clearly noticed from Table 2 that the resistance values of TiAl–Cr and TiAl–Cr–Mo alloys are much higher than the remaining two alloys. Accordingly, the corrosion film formed on TiAl–Cr–Mo alloy has the best protective ability, while that formed on TiAl–Mn alloy exhibits the worst.

The value of  $Q_f$  associated with the active area can provide evidence of the roughness of the corrosion film [33]. That is, the higher  $Q_f$  value of TiAl–Mn alloy makes its corrosion film rougher as compared to TiAl–Mn–Mo alloy. Additionally, the  $R_{ct}$  values are higher than the  $R_f$  values in both cases, suggesting that

**Table 2.** Values of the electrical equivalent circuit (EEC) fitting parameters for EIS data of TiAl alloys in 3.5% NaCl solution

Fitting parameters	Ti–48Al–2Cr	Ti–48Al–2Cr–2Mo	Ti–48Al–2Mn	Ti–48Al–2Mn–2Mo
$R_s, \Omega \text{ cm}^2$	27.25	33.78	16.58	18.14
$Q_f, \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$	–	–	$2.86 \times 10^{-5}$	$2.05 \times 10^{-5}$
$n_f$	–	–	0.88	0.90
$R_f, \Omega \text{ cm}^2$	–	–	42.9	75.3
$Q_{dl}, \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$	$6.32 \times 10^{-5} (Q_{CPE})$	$3.61 \times 10^{-5} (Q_{CPE})$	$1.47 \times 10^{-5}$	$1.39 \times 10^{-5}$
$n_{dl}$	0.83 ( $n_{CPE}$ )	0.89 ( $n_{CPE}$ )	0.83	0.78
$R_{ct}, \Omega \text{ cm}^2$	3645.2	5651.6	162.3	214.6
Chi-square ( $\lambda^2$ )	$2.14 \times 10^{-3}$	$4.41 \times 10^{-3}$	$1.28 \times 10^{-4}$	$2.76 \times 10^{-4}$

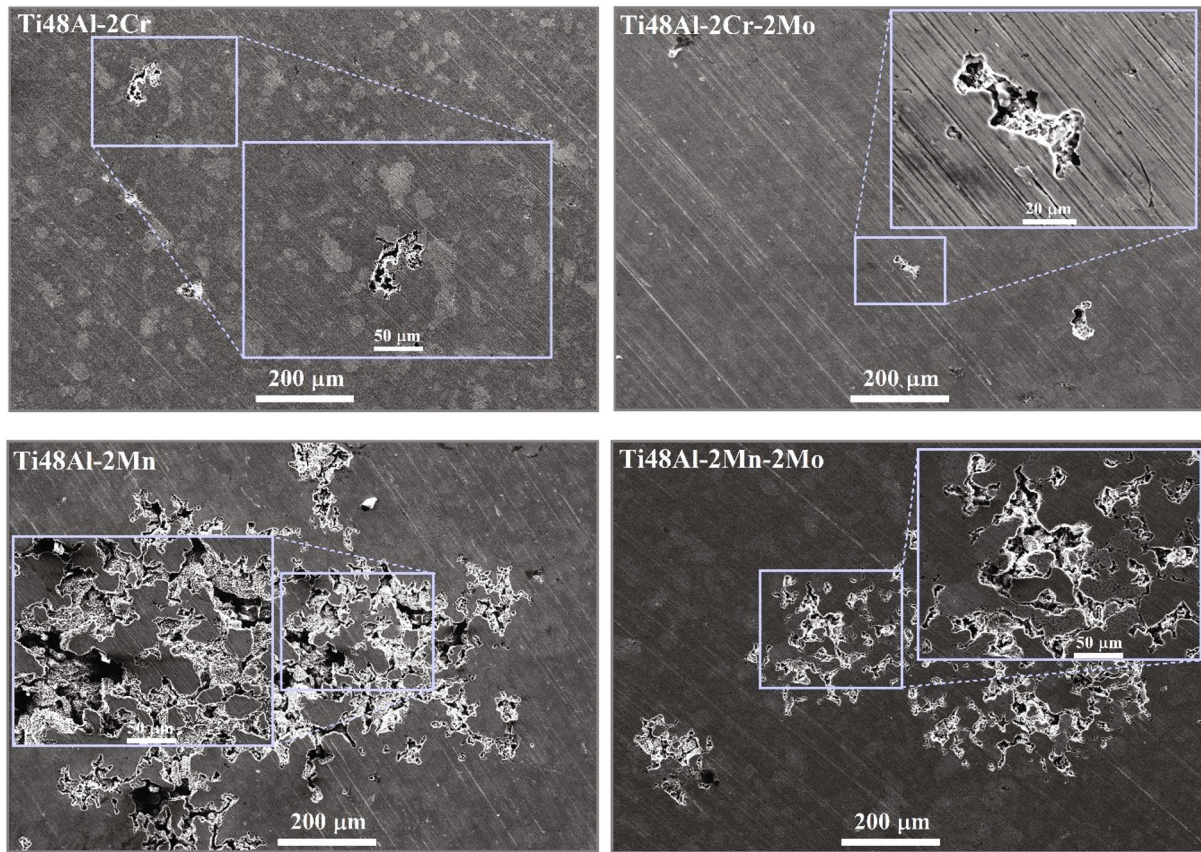


Fig. 7. Surface morphologies of TiAl alloys after potentiodynamic polarization tests in 3.5 wt % NaCl solution.

the inner layer presents a better resistance to chloride attacks.

SEM studies were performed to observe the results of the responses of TiAl alloys to NaCl solution. Figure 7 put forwards the surface morphologies (Secondary electron imaging (SEI)) of the alloys after the polarization tests in 3.5 wt % NaCl solution. Many corrosion pits with different shapes and sizes are clearly visible on corroded surfaces of all alloys, which are especially notable for the TiAl–Mn and TiAl–Mn–Mo alloys. It should be mentioned that the microstructures are represented by two different phases; the first region which is dark gray belongs to the TiAl phase and the second one is the light gray region which corresponds to the  $Ti_3Al$  phase. In the binary TiAl system, the  $Ti_3Al$  ( $\alpha_2$ ) phase contains 22–39 (at %) Al, while the TiAl ( $\gamma$ ) phase has Al content between 48.5 and 66 (at %) [34]. In addition to these phases, Mo-containing TiAl alloys have also TiAl phases that are rich in Mo. The composition of Mo-rich phases was reported to be 49.4Ti–43.1Al–2.1Cr–5.4Mo for TiAl–Cr–Mo alloy and 41.1Ti–52.8Al–1.4Mn–4.7Mo (at %) for TiAl–Mn–Mo alloy [4]. According to Fig. 7, the  $Ti_3Al$  phase appears to be more prone to corrosion because most of the corrosion pits are distributed upon it. Thus, this reveals that

the corrosion damage occurred more dramatically for the  $Ti_3Al$  phase. This fact may be an indication that the  $Ti_3Al$  phase is damaged as a result of selective corrosion. However, the effect of  $O^-$  and  $Cl^-$  ions on the corrosion process of TiAl and  $Ti_3Al$  phases needs to be further investigated. On the other hand, Fig. 7 confirms that the alloying strategy has a central role in affecting the number density of corrosion pits. TiAl–Cr and TiAl–Cr–Mo alloys are inferred to have enhanced surface morphology as compared to the remaining alloys due to the fact that they show the tendency of decreasing the number of corrosion pits. Moreover, the size and depth of the pitting holes on the surface of both mentioned alloys are smaller than those of TiAl–Mn and TiAl–Mn–Mo alloys, indicating that the alloys have different passivation characteristics. A study has been reported by Wu et al. [35], which highlighted that a thicker passive film was effective in ameliorating the pitting resistance of steel in chloride electrolyte. However, the aggressive chloride ions attack the corrosion film constituted on the surface and attempt to break it down, and once the passive film is damaged, pit nucleation and growth occur more easily on the surface. It has been proposed that Mo may play an important role in more than one step in a pitting process. Mo element changes the polarity

of the passive film by the formation of insoluble Mo compounds: the appearance of  $\text{MoO}^{n-}$  ions in the outmost part of the passive film modifies its intrinsically anionic selectivity into a cationic one, producing the development of a bipolar layer [15]. It encourages the diffusion of  $\text{O}^{2-}$ , and hence  $\text{Cr}_2\text{O}_3$  formation [36–39] and also impedes  $\text{Cl}^-$  entrance making the passive film more stable against corrosion attacks [40]. Moreover, Mo facilitates the repassivation behavior and blocks the growth of corrosion pits [38, 41]. The results of the work performed by Ilevbare and Burstein [41] featured that additional Mo to the stainless steel lowered the number and size of both nucleation and metastable pits, reducing the probability of forming stable corrosion pits. The literature data showing that the Mo element presents better protection from  $\text{Cl}^-$  attack which confirms the results of our study. Additionally, the accounted for possible mechanisms behind the positive effect of Mo addition are also thought to hold true for the alloys investigated here.

### CONCLUSIONS

In this work, the corrosion properties of four series of TiAl alloys with the compositions of Ti–48Al–2Cr, Ti–48Al–2Mn, Ti–48Al–2Cr–2Mo and Ti–48Al–2Mn–2Mo in 3.5 wt % NaCl solution were comparatively studied through electrochemical techniques. The corrosion behaviors of these alloys were observed to be significantly affected by Cr, Mn and Mo additions. The following main conclusions can be drawn from the above work:

(1) Mn addition showed a harmful effect on the corrosion resistance of TiAl alloy investigated in 3.5 wt % NaCl solution. Its presence dramatically increased the corrosion rate of the alloy, reaching the highest  $R_{\text{corr}}$  value of 0.3952 mm/year as well as the lowest  $R_p$  value of 1.33  $\text{k}\Omega \text{ cm}^2$ .

(2) With the addition of Mo, TiAl alloys exhibited an improved corrosion performance, and TiAl–Cr–Mo alloy presented the highest corrosion resistance to NaCl solution, with the least  $R_{\text{corr}}$  value of 0.1153 mm/yr.

(3) TiAl–Cr–Mo alloy offered good corrosion resistance, exhibiting a higher phase angle, larger semi-arc diameter, and greater charge transfer resistance ( $R_c$ ), which could be determined by the electrochemical impedance spectroscopy (EIS) tests.

(4) The corroded surfaces bore the features of pitting corrosion. In the case of TiAl–Mn and TiAl–Mn–Mo alloys, the number density of corrosion pits was significantly higher.

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### CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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