Loading influence on the corrosion assessment during stress-induced martensite reorientation in nickel-titanium SMA

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Abstract

The effect of stress-induced martensite reorientation on the corrosion behavior of a nickel-titanium (NiTi) shape memory alloy (SMA) was characterized by mechanical-electrochemical techniques. This martensite reorientation influenced the passive state of NiTi SMA. These passive to active state transitions could be sensed by the global interfacial electrochemical measurements, such as electrochemical impedance spectroscopy (EIS), open circuit potential (OCP) and linear polarization resistance (LPR) methods. The increase in the loading when exposed to a corrosive environment resulted in the breakdown of the passive layer. A later repassivation stage was reached due to the formation rate becoming more dominant than the breakdown rate during loading conditions. The integration of the mechanical loading by tensile testing, strain distribution by digital image correlation (DIC) and electrochemical methods by OCP and EIS, characterized and detected the influence of the mechanical effect in the corrosion assessment and interfacial mechanisms.

Keywords: shape memory alloy, corrosion, martensite reorientation

(Some figures may appear in colour only in the online journal)

1. Introduction

Shape memory alloys (SMAs) are a class of active materials with the capability to undergo and recover large deformations upon subjection to certain external stimuli, i.e., temperature and mechanical load. This capability has roots in a martensitic transformation, a solid-to-solid, diffusionless phase transformation between austenite and martensite. Upon loading, SMAs initially in the austenitic phase undergo phase transformation and recover the resulting strain upon unloading (pseudoelasticity). If initially in a martensitic phase, they undergo detwinning/reorientation upon loading. The apparent permanent strain after unloading can be recovered, and SMA can return to the original shape by subsequent heating (shape memory effect) \cite{1}. Due to these unique mechanisms, SMAs, such as nickel-titanium (NiTi), have found applications in the biomedical, automotive and aerospace industries \cite{2,3}.

Despite an endless potential use for this alloy, the application of SMAs has been limited by a lack of knowledge about their failure behavior, which has become a key factor to
fulfill safety and reliability requirements. Studying the failure mechanisms of SMAs is rather challenging because of the effects of phase transformation/reorientation and the inherent thermomechanical coupling. Despite this, there has been a recent rising interest in investigating the effects of the aforementioned phenomena on the failure of SMAs [4, 5]. The role of corrosive environments in the failure behavior of SMAs has been investigated [6–9]. Several studies have considered the impact of corrosive environment on performance of NiTi SMAs by measuring the change in fatigue lifetimes and studying the fracture surface. Shen et al [6, 10] studied the impact of a corrosive environment on the fatigue lifetime for NiTi wires subjected to rotational bending and recorded the number of revolutions before fracture. Their study was qualitative in nature when they showed multiple crack origins during fatigue cycles, but there were no details about a correlation between the formed cracks with a corrosion mechanism. Cheung et al [8, 9] expressed the fatigue life of NiTi in a chlorine-containing solution as a function of strain amplitude at the surface. They reported the formation of corrosion pits as a result of localized attack by sodium hypochlorite. Likewise, Lagoudas et al [11, 12] investigated the influence of corrosion on the failure of SMAs and reported a significant reduction of fatigue life in the presence of a corrosive environment. Their study suggested that this reduction in lifespan was due to a brittle surface oxide layer formed in such an environment. Racek et al [13, 14] investigated the mechanism of corrosion of NiTi during cyclic mechanical loading. They developed a new setup for an in situ electrochemical study of superelastic NiTi wires/springs in body fluids during cyclic mechanical loading. However, by having a U-bend or spring NiTi as part of the setup that led to a synergic action, the correlation of load versus electrochemical process was not covered. It is important to notice that most of existing studies on the corrosion of SMAs pertain to mechanical failure analysis and general corrosion in the presence of cyclic loading, rather than the influence of surface/electrolyte mechanisms on the corrosion assessment. There is a strong need to investigate the role of transformation/reorientation on the corrosion behavior of SMAs due to its influential effect of the surface during electrochemical processes, such as active and passive states, where the latter leads to an integral characterization of corrosion assessment.

In this paper, we investigate the effects of mechanical loading and martensite reorientation during a corrosion assessment for NiTi SMAs. Following an electrochemical cell set up designed to characterize the interfacial response while mechanical loading is imposed, experimental techniques coupled with imaging and high-resolution surface analysis helped to quantify parameters describing the passive-active state properties. The relationship of constant load versus interfacial characterization gave important insight for understanding SMA performance in a corrosive environment. To the best of the authors’ knowledge, this is the first time that multiple nondestructive in situ measurements have been reported to characterize the impact of an NiTi SMA crystallographic reorientation during a corrosion assessment. This includes an investigation on the changes in the passive oxide layer during stress-induced martensite reorientation by using digital image correlation (DIC) along with OCP and EIS techniques.

2. Experimental

2.1. Material characterization

The NiTi specimens utilized in this study were provided by ATI Inc., we cut 4 mm² samples from an as-received commercial equiatomic NiTi in a sheet form. A Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) was utilized for measuring the phase transformation temperatures [15].

Figure 1 shows the DSC curve for the heating and cooling of the sample. The exothermic and endothermic DSC peaks on cooling and heating are characteristics of the forward and reverse martensitic transformation of NiTi, respectively. The tangent method was used to obtain martensite start (Mₐ) and martensite finish (Mₐ) temperatures during cooling and austenite start (Aₘ) and austenite finish (Aₘ) temperatures during heating [1]. The transformation temperatures on figure 1 indicate that the material state at room temperature was fully martensite.

For mechanical characterization, a flat ASTM E8/E8 M sample [16] with a gauge length of 60 mm and a width of 9 mm were cut by using electrical discharge machining (EDM). The uniaxial tensile test was carried out at room temperature in a servo-hydraulic MTS test frame equipped with a 100 kN max load cell. Tension was applied to the sample with a loading rate of 0.2 mm min⁻¹ until failure.

2.2. Experimental design

In this study, the corrosion behavior of martensitic NiTi SMA was studied under an isothermal loading condition due to a microstructure reorientation. The mechanical properties of the NiTi SMA were evaluated by using a uniaxial tensile test in
Figure 2. Stress-strain curve of the NiTi sample with an initial martensite phase.

The detwinned/reoriented martensite region was determined with tensile test results (figure 2).

Figure 2 plots the engineering stress-strain curve for NiTi at room temperature. Since room temperature was below $M_s$, the material was in a twinned martensitic state at zero load. Upon loading, the twinned martensite was elastically deformed up to $\sim 1\%$ strain. A deviation from linearity was observed at close to 200 MPa, indicating the start of the detwinning/reorientation process. Given that a stress plateau can involve both twinning and detwinning, as well as some slip/plastic deformation [17, 18], the term ‘reorientation’ is used for the rest of this article. A stress plateau was observed at $\sim 240$ MPa during which the deformation was dominated by a reorientation of martensite variants. At the end of reorientation (approximately 4\% strain), reoriented martensite predominantly deformed elastically. This was followed by the start of plastic deformation at approximately 600 MPa, after which the deformation was dominated by slip plasticity with final failure of the material at close to 900 MPa [15, 19–21].

Due to the presence of nonlinear deformation mechanisms, the specimen underwent a large elongation (more than 60\%). The corrosion measurements were conducted at different load levels ranging from an elastic region of twinned martensite to a detwinned martensite ($\sim 240$ MPa), and then up to a plastic flow of a mechanically detwinned martensite. A schematic of the load steps is shown in figure 3. Different load steps were chosen to study corrosion behavior of the elastic deformation of twinned martensite (from point 0 to point 3), inelastic martensite reorientation (from point 4 to point 5), elastic deformation of detwinned martensite (point 6) and plastic deformation of detwinned martensite (point 7).

The values of stress and strain at each step are presented in table 1.

The corrosion response of the SMA material was evaluated using electrochemical methods. The electrode kinetics at different load levels was studied by using the following sequence of techniques.

- Open Circuit Potential (OCP): The value of OCP can be used to characterize the active or passive nature of the surface at the electrolyte/substrate interface over time. The surface can undergo an active state (metal dissolution), a passive state, or a mix of both states over time [22].
- Linear Polarization Resistance (LPR): The polarization resistance is a technique that characterizes the surface activation conditions on the interface by assuming that the charge transfer resistance is inversely proportional to the corrosion rate, which can be used to determine the surface active state of the NiTi sample under constant mechanical loads.
- Electrochemical Impedance Spectroscopy (EIS): EIS is a technique based on a transfer function principle including the introduction and measurement of a small current/potential amplitude in an electrochemical system. The spectra evolution with different loading reflects the interfacial mechanisms and characterizes the corrosion of the alloy surface. The oxide film formation and breakdown characteristics (charge transfer and mass transfer mechanisms) can be studied by utilizing a small amplitude alternating current (AC) source. EIS technique follows the linear system theory in which electrical passive elements can be used to characterize each element of the electrochemical system formed by associating each element with either charge transfer, mass transfer or simply the properties of the materials [23].
- Electrochemical Frequency Modulation (EFM): The spectra evolution with different loading reflects the corrosion progression of the electrode surface. EFM is a nondestructive method that applies a simultaneous dual-frequency potential wave to a metallic sample. The quality of results and validity of the EFM measurements can be verified by the experimental values of causality factors [24, 25].

A surface characterization was implemented by using a JCM-6000Plus Versatile Benchtop scanning electron
microscope (SEM). The surface was examined before exposure to corrosion and following electrochemical testing.

2.3. Experimental methodology

2.3.1. Imaging method. Digital image correlation (DIC) was used to measure the 2D strain field on the gauge section. To this end, white spray paint was first applied to the specimen surface. Black speckles were then sprayed on to produce a random pattern. Images were recorded with a rate of 1 Hz and using a Point Gray camera fitted with a Tokina ATX Pro lens, resulting in an optical resolution of 0.037 mm/pixel. The DIC subset size was selected as a $21 \times 21$ pixel based on the strain error (<0.1%) from the rigid body translation experiment; the step size was five pixels. The recorded images were postprocessed using Vic-2D-6 software provided by Correlated Solutions. Further details on DIC can be found in another [26].

2.3.2. Electrochemical testing methods. To investigate the interaction between mechanical and surface effects due to chemical dissolution effects, a uniaxial pseudostatic tensile test was performed for an ASTM E8/E8 M sample in a modified Ringer’s solution with a composition of 9.0 g l$^{-1}$ NaCl, 0.42 g l$^{-1}$ KCl, 0.24 g l$^{-1}$ CaCl$_2$ and 0.2 g l$^{-1}$ NaHCO$_3$. A metallic ASTM tensile sample was the working electrode. A graphite rod as the counter electrode and a saturated calomel electrode with a Luggin capillary as the reference electrode [28, 29]. A metallic ASTM tensile sample was the working electrode. The sequence of experiments included the immersion of the specimen in the electrolyte for 30 min prior to mechanical testing in order to reach a dynamic steady state condition.

The OCP was measured with respect to time during loading conditions. Measurements were performed with a Gamry Instrument Potentiostat/Galvanostat (600+). The OCP was continuously measured at each load level until stable potential values were achieved. The other electrochemical techniques (EFM, LPR and EIS) were carried out upon reaching a stable potential at time $t_0$ (immediately after the achievement of a stable potential value) and at each load level.

EIS measurements were carried out at the open circuit potential with an amplitude of 10 mV in a frequency range of 10 kHz to 30 mHz. EFM was carried out using two frequencies, 2 and 5 Hz, and a perturbation signal with an amplitude of 10 mV [25]. LPR was performed as the last electrochemical method at each load step in order to avoid the negative effects of potential perturbation and polarization on the EFM and EIS methods. The selected potential range was $\pm 20$ mV from stable potential values achieved during the incubation period. The scan rate employed for the LPR test was 0.125 mVs$^{-1}$.

3. Results and discussion

Figure 5 represents the open circuit potential of the SMA specimen measured continuously during a pseudostatic applied loading in a Ringer’s solution and at different stress and strain levels.

In the elastic deformation stage of twinned martensite (from point 0 to point 3), the open circuit potential remains constant ($-189 \pm 2.5$ mV versus SCE). There are quick drops in the OCP of the metal alloy that coincide with the martensite reorientation region (point 4 and 5), the elastic deformation state of detwinned martensite (point 6) and the plastic deformation of detwinned martensite (point 7). The steep drop indicates a transition to an active dissolution state on the surface of the metal alloy. Upon increasing the applied load, the OCP drops quickly and then gradually reaches a relatively steady-state value at the end of each increment. The potential magnitude indicates the activation and repassivation stages when the alloy faces loading conditions.

Figures 6(a) and (b) show the SEM images from the surface of the sample before and after the experiment, respectively. Figure 6(b) shows an active site formed on the surface due to the applied stress and the corrosive environment. Extensive cracking is found on the surface after applying stress. This shows that a passivity breakdown has taken place by applying a load and reaching roughly a 20% strain level. Spots of dark pores formed on the surface can be observed on the surface of NiTi-SMA following the electrochemical/mechanical testing. The latter is in accordance with previous works on the formed passive layer in the elastic stress state, and the passivity breakdown and localized attack susceptibility in chloride solutions [30–32]. A passive film formed in the presence of elastic stress has a higher donor and acceptor concentration than that of a passive film formed in a stress-free state. The higher concentration of acceptor and
donor sites promote the local attack susceptibility and breakdown of the passive film in an elastic stress state [33].

Table 2 shows the EDS results of the as received material and the material after corrosion testing. The EDS analyses reveal an increase in the ratio of Ti/Ni from 3.92 for as-received NiTi to 4.34 for NiTi after corrosion testing. This trend has been reported in previous studies [34, 35]. The passive film breakdown and subsequent repassivation influence the titanium content in the passive film. The chemical ratio increases for the titanium content takes into consideration some sites where the activation and repassivation are occurring, while the rest of the surface coverage maintains the layer at steady state conditions.

The EIS measurement results in Ringer’s solution at different stress levels are shown in figures 7, 8.

In the EIS signature plot (figure 7), the logarithm of the impedance and phase shift are plotted with respect to the logarithm of frequency. The EIS plots at medium and low frequencies represent the response associated with mechanisms occurring in the passive layer and interfacial reactions at the substrate/solution interface, respectively. Figure 7 gives the phase angle signature from the NiTi sample at different loading conditions while under continuous strain and exposed to Ringer’s solution. For different stress levels, the phase angle magnitudes of the impedance response at medium frequencies are close to 80 degrees. The above magnitude resembles a pseudocapacitance behavior that can be attributed to a dense passive oxide film, such as titanium in steady state conditions [36–38].

The phase angle magnitude decreases slightly during different stress levels between point 0 to point 6 followed by a slight increase. The latter could be due to a passivation and repassivation process. The phase magnitude at medium frequencies illustrates the stability of the passive layer formed, while the total impedance at low frequencies in figure 7 illustrates the charge transfer process at the interface. The formed passive layer on the surface of the NiTi sample is composed mainly of titanium oxide (TiO$_2$) with a small mixture of nickel [38]. The composition of the passive layer formed during oxidation of the titanium alloy is directly related to the alloying elements and temperature. The presence of NiO and NiTiO$_3$ in addition to the TiO$_2$ has been reported as the temperature increased to above 700 °C [39, 40].

Figure 8 shows the Nyquist plot representations for the NiTi SMA at different loads as previously described. In the Nyquist plots, the negative imaginary part of impedance is plotted versus the real impedance. The Nyquist plot is used to create an electrically passive analog circuit that characterizes an electrochemical system. The predominant mechanism is a charge transfer at the interface due to the dissolution of the metallic alloy in the corrosive environment. The passivation and repassivation is based on the interfacial reactions and layer breakdown occurring when the constant load is applied. The semicircle magnitude denotes surface activation (charge transfer mechanism) as the load increases. The last stress level $\sigma_7$, $\varepsilon_7$ indicates the lowest impedance magnitude. The diameter of the semicircle decreases when the load (stress) is higher. The latter takes into consideration the charge transfer mechanism being influenced by the activation or creation of active sites and the passivation-repassivation process. The semicircle magnitude agrees with the phase angle trend in which the passive layer breaks down (surface activation) and produces defects allowing the electrolyte into the passive layer.

The electrochemical system can be characterized by an equivalent circuit analog to qualitatively and quantitatively assess the effects of the stress level and the martensite reorientation influencing the active-passive corrosion behavior of NiTi in Ringer’s solution. The electrochemical elements are represented as electrical passive elements illustrated in figure 9. The proposed electric equivalent analog includes a solution resistance, $R_{\text{electrolyte}}$, in series with a parallel circuit of a constant phase element (representing a passive layer and pore resistance), $R_{\text{pore}}$, and finally a resistance representing the charge transfer process $R_{\text{polarization resistance}}$ and a constant phase element (CPE) for the interface between the passive porous layer with the metallic substrate. The $R_{\text{polarization resistance}}$ can characterize the surface activity and corrosion resistance under various stress levels.

Table 1. Stress and strain value of the NiTi dog bone at different load steps.

| Load step | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------|---|---|---|---|---|---|---|---|
| Stress (MPa) | 0 | 160 | 178 | 190 | 232 | 244 | 386 | 683 |
| Strain (%) | 0 | 0.36 | 0.45 | 0.52 | 0.9 | 3.8 | 7.4 | 18.8 |
| Material state | Tw | Tw | Tw | Tw | Tw & DTw | Tw & DTw | DTw | DTw |

Tw: Twinned Martensite.
DTw: Detwinned Martensite.

Figure 5. OCP of NiTi-SMA in a Ringer’s solution during pseudostatic loadings.

![Image](image.png)
The CPE parameter is defined as [38, 41]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^\alpha}$$

(1)

where $Y_0$ is a constant in S cm$^{-2}$s$^{-\alpha}$ and $\alpha$ is related to the angle of rotation of a purely capacitive line on the complex plane plots.

The CPE represents a parameter that characterize an electrochemical surface by considering the physical properties of the surface. The alpha parameter correlates to the roughness of the surface and represents the forming of a dense and packed dielectric material when it is close to one. In addition, porosity and decreased compactness influence the magnitude close to zero, turning the surface into a resistor when the porosity permits current leakage through the system.

The values of the electrochemical equivalent circuit elements obtained for each stress level are presented in Table 3. $\alpha_1$ and $\alpha_2$ represent the exponent values for the CPE element due to the passive or barrier layer and substrate-passive layer interface respectively.

The solution resistance remains constant and does not change after applying various loads on the metallic sample. There is a decrease in polarization resistance upon applying load, which can be related to the passivation-breakdown of the oxide layer. This layer is mainly composed of TiO$_2$ [41]. A decrease can be observed in the polarization resistance ($R_p$) values when the applied loads increased. The formed corrosion product could lose adhesion in some local sites during loading conditions and reorientation. This loss in adherence is associated with changes in the abovementioned potential due to the surface characteristics [42]. $R_{ct}$ magnitudes from 160 k$\Omega$ to 49 k$\Omega$ denote higher current exchange at the interface.

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**Figure 6.** SEM images from the surface of (a) as received NiTi-SMA and (b) after corrosion testing in Ringer’s solution during pseudostatic loading at room temperature.

**Figure 7.** Bode plots of the NiTi SMA specimen under different stress levels in Ringer’s solution at room temperature.

**Figure 8.** Nyquist plots of the NiTi SMA specimen under different stress levels in Ringer’s solution at room temperature.

|                | Nickel (at%) | Titanium (at%) | Oxygen (at%) | Titanium/Nickel |
|----------------|-------------|----------------|--------------|-----------------|
| As-received    | 14.49       | 56.80          | 28.71        | 3.92            |
| After corrosion testing | 13.90       | 60.32          | 25.78        | 4.34            |

**Table 2.** Surface analysis of NiTi-SMA, before and after corrosion testing in Ringer’s solution.
due to an increase in active or dissolution sites following the passive layer breakdown and repassivation at the substrate/barrier oxide interface. The pore resistance agrees with the active-passive behavior of the passive layer where the physical properties of the layer are modified during the loading conditions. Due to an increase in nickel content within the layer following loading conditions, as illustrated in table 3, the resistivity dropped and the porosity could be increased, with the pore resistance decreasing from 140 Ω to 100 Ω.

Figure 10 shows the capacitance magnitude for the oxide layer measured by using CPE element parameters and the thickness based on expression 3.

The capacitance of the oxide layer associated with the CPE element is given by [43]:

\[ C_{ox} = \left( Q_{oxide\_layer}\right) \alpha R_{pore} \frac{1-\alpha}{\alpha} \]  

(2)

where Q, R and m are estimated by the CPE element expression.

The thickness of the surface oxide layer has been calculated to form the values of the capacitance oxide layer according to the following relation:

\[ d = \frac{\varepsilon \varepsilon_0}{c_{ox}} \]  

(3)

where \( \varepsilon \) is the dielectric constant of the titanium oxide (100), \( \varepsilon_0 \) is the permittivity of free space (8.854 × 10^{-12} F cm^{-1}) and \( c_{ox} \) is the capacitance of the oxide layer [43, 44].

The comparison of the capacitance of the oxide layer and the thickness of the oxide layer is presented in figure 10. This trend is influenced by the loading introduced to the sample. The capacitance shows a decrease in magnitude, which is considered to be a current leakage when the capacitance is no able to store charges, rather than the current passing within the more conductive or defect interface or the substrate-passive interface. The latter might include the deterioration of the mechanical physical properties of the passive layer, or bonding with the substrate. The displayed thickness shows a decrease in magnitude. The layer not only shows a pathway for the current but also less resistance due to pore formation or breakdown as previously explained.

The passive layer changes can be correlated to inelastic deformation and strain distribution on the surface.

The strain distribution in the loading direction (\( \varepsilon_{yy} \)) for the ASTM E8/E8 M specimen subjected to uniaxial tension was measured using DIC and is presented in figure 11(c). The contour plots correspond to overall uniaxial strain values from 1% to 4% (figure 11(a)) during which the martensitic NiTi undergoes martensite reorientation [45, 46]. According to the images, the strain distribution is nearly uniform throughout the specimen at the beginning. As the loading continues, strain bands oriented at approximately 45 degree, with respect to the loading direction, start to appear throughout the specimen. The localization becomes more pronounced near the bottom of the specimen at 1.7% strain. Further loading results in the broadening of the strain localization band at the bottom, and more pronounced localization of the band near the top at 2.5% strain. The bands then coalesce, and again a nearly uniform distribution is attained at 4% overall strain. The localized strain band would lead to a localized passive layer breakdown due to reorientation. The changes in the OCP are shown in figure 11(b). The existence of potential drop upon loading at the beginning of reorientation is related to changes on the strain filed on the surface.

Figure 12 shows the schematic of the passive layer changes and illustrates the passive layer breakdown and formation of a new passive layer. A stable passive layer exists on the surface of twinned martensite. The localized passive layer breakdown occurs during the martensite reorientation due to the strain localization (b) and active dissolution sites formed on the surface. It is worth noting that while a majority of the sample experiences strains in the range 1%–2%, local strains can go up to 4% due to martensite reorientation. These large strains can lead to failure of the brittle passive oxide layer on the surface. The metal dissolution rate increases inside the localized breakdown (c) and a new passive layer starts forming on the surface of the NiTi detwinned martensite.

To further corroborate the performance of the interface, the polarization resistance values and the corresponding Ecorr values served as a function of the strain in a Ringer’s solution, as shown in figure 13. The results indicate that there is an
important change in $E_{\text{corr}}$ values based on two different regions (elastic-plastic) and crystallographic transition (twinning-detwinning). The beginning of the deformation is the most influential parameter in the formation of the passivation layer at the surface of the substrate. Castaneda et al. [47] describes the influence of the strain rate on the mechanical breakdown of a formed passive layer. The strain rate is faster than that of the formation of the layer at the local attack sites; this latter favors and influences the passive layer breakdown. The OCP and the $R_p$ are increasing with stress within steps 0 to 6 (table 1), validating the influence of the elastic region for twinned martensite in the stress-strain curve.

As shown in figure 13, at the beginning of the reorientation, the rate of change of $R_p$ and LPR with the applied strain stays constant within the elastic twinned martensite region. Additionally, figure 13 indicates a drop in the OCP potential in the same region. This result indicates that in the martensite reorientation process the metal/solution interface shifts towards a more active condition while the corrosion rate increases. The latter can be related to the breakdown of the layer being faster than that of the passivation formation, as well as the mechanical effect on the passive layer bonding at the interface influences the activation of the substrate surface.

Upon mechanical loading up to the inelastic region and after the martensite reorientation region, the $E_{\text{corr}}$ values stay relatively constant, but the LPR and $R_p$ slopes decrease monotonically with the applied strain. The behavior of the polarization resistance results across this range of applied strain suggests that, after martensite reorientation, the passive layer breakdown in some regions makes a porous layer where active sites are formed, and charge transfer reactions occur during the martensite reorientation. The available sites on the porous layer are due to the passive layer breakdown and show an activation control mechanism at the interface. Both LPR and OCP magnitudes validate the correlation of loading versus surface activation in this solution.

Figure 14 shows the calculated Tafel constants at each stress level by EFM techniques. The Tafel constants are calculated by using the current peaks obtained at the harmonic and intermodulation frequencies. The experimental values are the causality factors (CF-2 and CF-3) obtained during each EFM measurement. The mathematically established theoretical values of CF-2 and CF-3 are 2 and 3, respectively. The calculated causality factor values are approximately equal to the theoretical values and show the measured EFM data are reliable. The derived equation for mathematical calculation of the Tafel constants and causality factors are provided in appendix [24].

As shown in figure 14, the anodic and cathodic Tafel slope values follow the same trend at the elastic region where the cathodic Tafel slopes are higher than the anodic ones. These results suggest that the anodic reaction kinetics (metal dissolution) are consistently faster than the corresponding cathodic reaction.

Under a uniform dissolution model, the trend followed by the cathodic Tafel slopes value are consistent with the results shown in figure 10, indicating the increase in the corrosion rate at the passive surface in open circuit conditions. As shown in the results presented in both figures 13 and 14, the shift to a more active condition coincides with the onset of the martensite reorientation and the loading conditions. The strain rate is faster than the repassivation kinetics; thus, the MO$_4$ layer becomes more susceptible to breakdown when the load is increased and the strain affects the surface and the passive layer bonding. Martensitic reorientation becomes negligible for the global classical EIS or DC measurement. The localized effect due to phase transition can be characterized by local electrochemical techniques and methods, but that is beyond the scope of this work.

The relative difference between the cathodic and anodic electrode kinetics as indicated by the Tafel slopes, suggest that particularly at higher strain levels (within the plastic region), localized attack (i.e., passive layer breakdown) is possible since at open circuit conditions the higher anodic reaction kinetics would need to be sustained by a slower cathodic reaction that occurs over a larger fraction of the exposed surface.

The collective result of the electrochemical tests performed indicates that as the strain applied on the specimen increases toward the plastic range (post reorientation) the passive layer produced by the alloy is broken down in an ability to reduce the general dissolution rate at the surface. The reduction in dissolution rate is due to an increase in anodic activity and is expressed as a corrosion attack.

### Table 3. The values of the electrochemical equivalent circuit elements from the results of EIS tests at various stress levels.

| Components                  | Stress level (MPa) |
|-----------------------------|--------------------|
| $R_{\text{electrolyte}}$ ($\Omega \text{ cm}^{-2}$) | 0 160 178 190 232 244 386 683 |
| $R_{\text{pore}}$ ($\Omega \text{ cm}^{-2}$)       | 1.78 1.9 1.7 1.7 1.8 1.6 1.6 1.5 |
| $R_{\text{polarization resistance}}$ (k$\Omega \text{ cm}^{-2}$) | 140.2 141.8 153.6 152.8 128.8 143.4 124.4 100.8 |
| $Q_{\text{barrier layer}}$ ($S \times s^2 \times 10^4$) | 1.52 1.85 5.58 5.66 6.57 6.55 7.5 10.4 |
| $Q_{\text{oxide layer}}$ ($S \times s^2 \times 10^4$)  | 0.77 0.76 0.75 0.75 0.76 0.75 0.75 0.74 |
| $\alpha_1$                  | 1.54 1.36 1.76 1.71 1.47 2.7 2.73 4.36 |
| $\alpha_2$                  | 1 1 0.95 0.954 1 0.97 1 1 |
4. Conclusions

The corrosion resistance of NiTi SMA is deteriorated during loading and martensitic reorientation. The corrosion assessment of NiTi SMA due to martensite reorientation and due to load conditions can be summarized as follows:

1. The OCP remains constant during deformation in the elastic region. The EIS and SEM results indicate and show the presence of a passive layer. The passive layer breakdown is influenced by the loading, and since the repassivation is slower than the breakdown rate, it results in the activation of the surface over time. The higher cathodic slope in the elastic region suggests that
the faster anodic reaction kinetics confirm the activation state.

2. Inelastic strain during martensite reorientation significantly increases the mechanical-electrochemical effect, which can be detected by quick drops at the open circuit potential. The metal/solution interface shifts towards a more active condition in the detwinning process by a reduction in polarization resistance values.

3. A quick drop at the OCP coincides with the plastic deformation of NiTi SMA. The change in the surface of the sample due to plastic deformation of detwinned

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**Figure 12.** Schematic of passive layer: (a) before martensite reorientation, (b) the passive layer breakdown at the start of the martensite reorientation, (c) the martensite reorientation, (d) and the formation of the new passive layer.

**Figure 13.** Variation of measured polarization resistance under different strain levels.

**Figure 14.** (a) Anodic and cathodic Tafel slope values obtained by electrochemical frequency modulation (EFM) for NiTi under different strain levels.
martensite leads to a decrease in the slope of the LPR line. This change in the slope of the LPR line shows the higher possibility of local attack during martensite reorientation and in plastic deformation regions.

Appendix

The over potential expression for a dual-frequency sinusoidal potential signal:

\[ \eta = U_0 \sin \omega_1 t + U_0 \sin \omega_2 t \]  

(4)

The substitution of equation (4) in the Stern-Geary expression results in:

\[
i = i_{corr} \left[ \exp \left( \frac{U_0 \sin \omega_1 t}{\beta_a} \right) \exp \left( \frac{U_0 \sin \omega_2 t}{\beta_a} \right) - \exp \left( \frac{U_0 \sin \omega_1 t}{\beta_c} \right) \exp \left( \frac{U_0 \sin \omega_2 t}{\beta_c} \right) \right]
\]

(5)

By using the Taylor series for exponential parts to the third order and invoking trigonometric relationships, equation (5) yields the following form:

\[
i = i_{fr} + i_{sc} \sin \omega_1 t + i_{sc} \sin \omega_2 t - i_{sc} \cos \omega_1 t - i_{sc} \cos \omega_2 t - i_{sc} \sin \omega_1 t - i_{sc} \sin \omega_2 t - i_{sc} \cos \omega_1 t - i_{sc} \cos \omega_2 t \]

(6)

where \( i_{corr}, \beta_a \) and \( \beta_c \) are obtained in the following form:

\[
i_{corr} = \frac{i_{w_1, w_2}^2}{2 \sqrt{8i_{w_1, w_2}i_{w_1, w_1} - 3i_{w_1, w_1}^2}}
\]

(7)

\[
\beta_a = \frac{i_{w_2, w_1, w_0}}{i_{w_2, w_1}i_{w_1, w_0}}
\]

(8)

\[
\beta_c = \frac{i_{w_2, w_1, w_0}}{i_{w_2, w_1}i_{w_1, w_0}}
\]

(9)

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