Effect of Heat Treatment of Martensitic Stainless Steel on Passive Layer Growth Kinetics Studied by Electrochemical Impedance Spectroscopy in Conjunction with the Point Defect Model

Ingmar Bösing *, Georg Marquardt and Jorg Thöming

Chemical Process Engineering, University of Bremen, Leobener Strasse 6, 28359 Bremen, Germany; gjm@gmx.de (G.M.); thoeming@uni-bremen.de (J.T.)

* Correspondence: ingmar.boesing@uni-bremen.de

Received: 27 January 2020; Accepted: 1 March 2020; Published: 3 March 2020

Abstract: Martensitic stainless steels are widely used materials. Their mechanical and corrosion properties are strongly influenced by their microstructure and thereby can be affected by heat treatment. In the present study, the effect of different austenitizing temperatures on the passive film growth kinetics of martensitic stainless steel is studied by electrochemical impedance spectroscopy. The data was further fitted by the point defect model to determine kinetic parameters. We show that an increasing austenitizing temperature leads to a more protective passive film and slows down passive film dissolution in sulfuric acid.

Keywords: passivity; stainless steel; electrochemical impedance spectroscopy; point defect model; heat treatment

1. Introduction

The passivity of stainless steel is one of the most important phenomena of our modern metal-based civilization [1]. Various studies over recent decades on stability [2–4], structure [5–7] and semi conductive properties [8–11] of passive films underline their significance in research and industry.

Heat treatment of materials can affect the microstructure and thus has not only a crucial effect on the mechanical properties but also on the corrosion properties [12]. The influence on the different corrosion mechanisms; however, is not easy to distinguish in many cases. For example, it is well known that austenitizing a martensitic steel can increase its hardness but the influence on corrosion behavior is still a matter of debate. Candelaria et al. showed that with increasing austenitizing temperature up to a critical temperature, the weight loss due to corrosion increases [13]. At higher austenitizing temperatures, the mass loss decreases again. In contrast, Rosemann et al. observed increasing critical pitting potentials with heat treatment temperature [14] indicating a better resistance against corrosion.

In a recent study, Bösing et al. showed that different corrosion mechanism are affected differently by the austenitizing procedure [12]. Several microstructure changes occur due to the heat treatment: Increasing temperature leads to the formation of martensite, the dissolution of iron carbides, to the dissolution of chromium carbides, the diffusion of chromium, and the growth of the former austenite grain size.

These microstructure properties can affect the passive layer and thus the corrosion behavior. An increasing martensite content leads to a more defective passive layer and an accelerated dissolution [15]. This is attributed to a higher lattice distortion due to the martensite crystal structure [13]. The dissolution of carbides increases the carbon content in the crystal structure which also leads to higher
lattice distortions and can increase corrosion. The dissolution of chromium carbides on the other hand increases the amount of chromium which is available for the formation of the passive layer.

It was shown that the lattice distortions, which increase with austenitizing temperature, lead to a decreasing pitting potential (the potential at which pitting starts), which indicates a higher susceptibility to pitting corrosion. Contrary to these findings, a decreasing corrosion rate and decreasing passive current could be observed. Both phenomena (decreasing corrosion rate and decreasing passive current) suggest slower corrosion during steady state and a more passivated surface. This behavior was addressed to the dissolution of chromium carbides and thus a higher amount of chromium in the passive film [12].

A description of passive film formation requires detailed information about the physioelectrochemical properties and reactions of the investigated system [16]. It has been frequently studied using the point defect model (PDM) [1,17–20]. This model describes oxide film growth by a set of interfacial reactions and transport of point defects through the film, which leads to the growth and decomposition of the passive layer. Macdonald et al. developed the PDM from its early beginnings in the 1980s [21] until today and added reactions for the dissolution of the passive layer, the formation of metal and oxygen interstitials as well as vacancies [19]. It was concluded that the rate-limiting step for film growth is the formation of anion vacancies at the metal/oxide interface, which is driven by the potential drop at this interface [19]. Since film growth is limited by interfacial potentials and electric field strength is assumed to be independent from the applied potential (because of the buffering action of band-to-band or band-to-interbandgap state tunneling [1]), the PDM is considered an interface model (IFM) that can reliably describe oxide growth. In 2002, Olsson et al. showed, by using a electrochemical quartz crystal microbalance, that oxide growth on stainless steel follows kinetics described by IFM rather than so-called high field models [22]. Such models assume the film growth to be limited by ion conductivity through the oxide and the electrical field across the passive film as a function of the applied potential [23].

In the actual PDM, the typical set of 7 interfacial reactions is used to describe various oxide layers on different metals, such as n-type oxides (through mainly oxide vacancies and metal interstitials) and p-type oxides (through mainly metal vacancies and oxygen interstitials) as well as the formation of defects by interfacial reactions [19]. The influence of heat treatment on passivation kinetics, however, has not been described yet.

In the present study we investigate the passive film growth kinetics of martensitic stainless steel samples which were heat-treated at different austenitizing temperatures. By analysis of electrochemical impedance spectroscopy (EIS) measurement and parameter optimization using the PDM, we explain the effect of austenitizing on the reaction kinetics at the metal/passive film interface in order to explore the effects of material treatment on corrosion behavior. To do this, we investigated a set of 6 stainless steel samples with different heat treatment. EIS measurements were performed using sulfuric acid for which the passive behavior of stainless steel is known to show a broad passive area that clearly distinguishes from the active/passive and transpassive region [24]. By a combination of comprehensive electrochemical measurements and modeling using a full as well as a reduced PDM film growth model, we gained new insight into the passivation processes that go beyond the findings of measurements alone.

2. Materials and Methods

2.1. Material and Sample Preparation

The stainless steel samples were produced at the Max Planck Institut für Eisenforschung (Düsseldorf, Germany) with a composition as listed in Table 1. The samples were heat-treated at 5 different austenitizing temperatures (\(T_A: 1000, 1050, 1100, 1150\) and 1200 °C) for 2 h and compared to an untreated sample (T0). The austenitizing time was chosen to ensure dissolution of the carbides and to provide time for the diffusion of chromium and for grain coarsening. The austenitizing temperatures were chosen to provide two temperatures below the dissolution temperature of Cr7C3 (1000 and 1050 °C), two temperatures around the dissolution temperature (1100 and 1150 °C), and
one temperature at which dissolution is ensured (1200 °C) [25]. Furthermore, due to the different austenitizing temperatures, the grain growth accelerates with increasing temperature [26,27]. By quenching with high temperature gradients (50 K/s), new carbide formation was excluded, and martensite formation was achieved. The samples were subsequently glued into a Polyvinyl chloride (PVC) embedding using two-component adhesive.

The X-Ray diffraction measurements were performed using a MZ IV diffractometer (GE Inspection Technology, Ahrensburg, Germany). For signal detection a position-sensitive detector “Miostar 2” (Photron-X) was used. Kβ-Filtration was carried out by using Vanadium filter. The measurements were performed with a scan step of 0.05°.

To determine the former austenite grain size, the samples were etched with a mixture of 1.5% picric acid, 10 drops of 100% hydrochloric acid and 0.9 g sodium dodecylbenzenesulfonate. The line intersect method was used to determine the grain size.

| Table 1. Element distribution of investigated stainless steel samples in ma.-%.
|---|---|---|---|---|---|---|---|
| Allying Element | C | Cr | Fe | Mn | O | P | S | Si |
| Laboratory alloy | 0.497 | 13.700 | bal. | 0.372 | 0.0033 | 0.0022 | 0.0031 | 0.0075 |

### 2.2. Electrochemistry

Each EIS measurement was repeated 3 times. Before each measurement the working electrodes (martensitic stainless steel samples, sample area: 0.785 cm²) were wet grinded with SiC grinding paper with grain sizes from 600 to 200 μm, degreased in ethanol, and cleaned in an ultrasonic bath containing deionized water.

All electrochemical measurements were carried out at room temperature using a standard three electrode cell using a Metrohm Autolab potentiostat (Utrecht, Netherlands) with the PGSTAT204 and the FRA32 modules. A platinum electrode served as counter electrode and a Ag/AgCl 3M KCl electrode as reference electrode, while the investigated material samples act as working electrodes. All potentials in this paper are referred to the Ag/AgCl electrode.

Linear sweep voltammetry (LSV) measurements were performed in 0.5 M sulfuric acid, the scan velocity was set to 100 mV/s, the starting potential was set to −500 mV, and the stop potential lies at 1600 mV. The high scan rate was chosen to show the last oxidation peak which does not occur at typical low scan rates.

The EIS measurements were also performed in 0.5 M sulfuric acid after polarization for 1800 s at 600 mV during which a passive layer was formed. The measurements were performed in the frequency range between 10⁵ and 10⁻² Hz with an AC amplitude of ±10 mVrms.

### 2.3. Fitting the Point Defect Model

The PDM [21] describes oxide film growth on metals by interfacial reactions and point defect transport through the film. The interfacial reactions as well as the defect transport are controlled by potential drops at the metal–film and film–solution interfaces and the potential drop over the film (Figure 1a).

Some additional assumptions were made in this manuscript to simplify the fitting of the impedance data to the model:

1. The passive layer solely consists of Me₂O₃ species, namely Fe₂O₃ and Cr₂O₃(which leads to χ=3 in the reaction scheme (Figure 1)).
2. The dissolution of the oxide layer does not lead to a change of oxide state of the metals and Me₂O₃ dissolves to Me³⁺ (Reactions 4, 5, and 7 do not play a role regarding the faradaic impedance).
3. The defects leading to the n-type structure of the passive film on stainless steel are oxygen vacancies. Hence, metal interstitials are neglected for the purpose of this paper and for simplification and so are Reaction 3 and 5. Both currents, produced by the formation of metal interstitials and by the formation of oxygen vacancies, cannot be distinguished and the
calculated rate constants could be composite of both reactions. To ensure n-type behavior at the
given potential Mott-Schottky-Analysis are done and can be seen in the supplementary materials
(Figure S1, Figure S2).

4. The inner barrier layer is the protecting passive layer and the reactions at the barrier layer-metal
interface are described by the PDM.

**Figure 1.** (a) Reaction mechanism at the metal–film and film-solution interface; at the metal–film
interface, the following reactions occur: the consumption of cation vacancies by metal atoms from the
metal (Reaction 1); the formation of metal ions inside the passive layer and oxygen vacancies
(Reaction 2); the formation of metal interstitials (Reaction 3); at the film-solution interface, the
following reactions occur: Dissolution of metal ions from the passive layer and generation of cation
vacancies (Reaction 4); metal interstitials inside the passive layer react to metal ions and dissolve to
the electrolyte (Reaction 5); oxygen vacancies react with water to oxide ions in the passive film
(Reaction 6) and the dissolution of the oxide film to metal ions in the electrolyte and water (Reaction
7). Following the Kröger–Vink notation: me: Metal atoms inside the metal, Me_{ox}: Metal ions inside the
oxide, V_{O}: Oxygen vacancies (two positive charges indicated by two dots), V_{M}^{2+}: metal vacancies,
O_{ox}: Oxygen ions inside the oxide; (b) Electrostatic potential as a function of distance from metal surface.
Potential drop at the interfaces: \( \varphi_{mf} \): potential drop at the metal–film interface; \( \varphi_{f} \): potential drop
inside the passive layer; \( \varphi_{fs} \): potential drop at the film/solution interface; \( U_{ext} \): external potential.

The model comprises two competing parallel electron-generating reactions and three non-
electrochemical reaction. The electrochemical reactions are Reaction 1 and 2, which describe the
consumption of metal vacancies and formation of metal ions in the oxide (Reaction 1) and formation
of the oxide by the production of metal ions in the oxide layer and oxygen vacancies (reaction 2). The
driving force of the electrochemical reaction is the potential drop at the metal–film interface \( \varphi_{mf} \). The
potential drop is equal to the external potential \( U_{ext} \) minus the potential drop over the passive film
\( \varphi_{f} \) (which is the product of the electric field strength inside the film and the film thickness, \( \varphi_{f} = E_{f}L \))
and the potential drop at the film-solution interface \( \varphi_{fs} \) (Figure 1b):
\[
\varphi_{mf} = U_{ext} - \varphi_f - \varphi_{fs}
\]

Please note that for various pH and/or various external potentials the nature of \(\varphi_{fs}\) must be considered in the model \(\varphi_{fs} = \alpha U_{ext} - \beta \text{pH} - \varphi_{fs}^0\). In the present case (constant pH and external potential) \(\varphi_{fs}\) can be considered to be a constant and can be combined with the base rate constant to form the standard rate constant: \(k_i^0 = k_i^{0*} \exp(-\varphi_{fs})\). The potential drop across the passive film can be calculated by the electric field strength inside the film \(E_F\) and the film thickness \(L\). By this, the rate constants \(k_1\) and \(k_2\) can be calculated as

\[
k_i = k_i^0 \exp \left( \frac{\alpha_i n_i F}{R T} (U_{ext} - E_F L - \varphi_{fs}) \right) = k_i^0 \exp \left( \frac{\alpha_i n_i F}{R T} (U_{ext} - E_F L) \right) ; i = 1, 2
\]

Here, \(k_i^{0*}\) represents the base rate constant of reaction \(i\), \(k_i^0\) stands for the standard rate constant of reaction \(i\), \(\alpha_i\) for the charge transfer constant of reaction \(i\), \(F\) for Faraday’s constant, \(n_i\) for the number of electrons involved in the reaction, \(R\) is the universal gas constant and \(T\) the absolute temperature. The admittance \(Y_F\) of the electrochemical system can be calculated by the total differential of the current [28]:

\[
Y_F = \frac{1}{Z_F} = \frac{\partial I}{\partial U} = \left( \frac{\partial I}{\partial U} \right)_{Lc_c} \frac{\partial U}{\partial U} + \left( \frac{\partial I}{\partial U} \right)_{C_c U} \frac{\partial L}{\partial U} + \left( \frac{\partial I}{\partial C_c} \right)_{L U} \frac{\partial C_c}{\partial U}
\]

Here \(Z_F\) is the faradyic impedance, \(I\) the current, \(U\) the potential and \(C_c\) the concentration of cation vacancies. The complete derivation of the admittance can be found in the original literature of Macdonald et al. – for example ref. [29,30].

The partial differential \(\partial L/\partial U\) can be neglected if the change of \(L\) is less than the atomic radius of the chromium and iron atoms in the oxide [30]. Adding an admittance for the oxide layer by a Constant Phase Element (CPE) yields

\[
Y_{tot} = Y_F + Y_{cap}
\]

With

\[
Y_{cap} = Y_{CPE} = Q(j\omega)^N
\]

where \(j\) is the imaginary number and \(\omega\) the angular frequency. The CPE parameters \(Q\) and \(N\) are related to the film thickness \(L\) by

\[
\frac{\varepsilon \varepsilon_0}{L} = Q(\omega_m'')^{N-1}
\]

with \(\omega_m''\) the frequency at which the imaginary part of the impedance has its maximum [31] and \(\varepsilon_0\), the permittivity of the vacuum \((8.85 \times 10^{-14} \text{ AsV}^{-1}\text{cm}^{-1})\) as well as \(\varepsilon\), the dielectric constant of the oxide \((\varepsilon = 12\) [32]). Combining Equation (3), (4), (5), and (6), the total admittance can be written as

\[
Y_{tot} = \left( \frac{\partial I}{\partial U} \right)_{Lc_c} + \left( \frac{\partial I}{\partial C_c} \right)_{L U} \frac{\partial C_c}{\partial U} + \frac{\varepsilon \varepsilon_0}{L(\omega_m'')^{N-1}} (j\omega)^N
\]

The partial derivative \(\partial I/\partial U\) can be found as

\[
\frac{\partial I}{\partial U} = 3F a_1 k_1 C_c + 3F a_2 k_2
\]

with \(a_i = \alpha_i n_i F / R T\). Differentiating the current \(I\) with respect to the cation vacancies concentration \(C_c\) yields

\[
\frac{\partial I}{\partial C_c} = 3F a_1 k_1
\]

The partial derivative \(\partial C_c/\partial U\) at the point \(x = L(\partial C_c/\partial U)\) can be derived by the flux of cations [30] and can be written as
with
\[
C_c^{U} = \frac{(b_{1V}a_{22} - b_{2V}a_{12})\exp(r_1L) + (b_{2V}a_{11} - b_{1V}a_{12})\exp(r_2L)}{a_{11}a_{22} - a_{12}a_{21}}
\]
(11)
\[
C_c^{L} = -a_{12}b_{2L}\exp(r_1L) + a_{11}b_{2L}\exp(r_2L)
\]
(12)

and
\[
r_{1,2} = \frac{3K \pm \sqrt{3^2K^2 + 4i\omega/D_v}}{2}
\]
(13)
\[
a_{11} = (r_1 - 3K)D_v; a_{12}(r_2 - 3K)D_v
\]
\[
a_{21}(r_1 - 3K)D_v + k_1]\exp(r_1L); a_{22}(r_2 - 3K)D_v + k_1]\exp(r_2L)
\]
(14)

By solving the differential equation for film growth (considering a constant \(H^+\) concentration \(k'_7C_{H^+} = k_7\)),
\[
\frac{dL}{dt} = \Omega k_2 - \Omega k'_7C_{H^+} = \Omega k_2^0 \exp\left(\frac{\alpha_2nF}{RT}(U_{\text{ext}} - E_FL)\right) - \Omega k_7
\]
(17)

with \(\Omega = 14.6 \text{ cm}^2\text{mol}^{-1}\), the molar volume of the oxide, it is possible to calculate the current film thickness \(L\)
\[
L = \int \left(\Omega k_2^0 \exp\left(\frac{\alpha_2nF}{RT}(U_{\text{ext}} - E_FL)\right) - \Omega k_7\right)dt
\]
(18)

The steady state film thickness \(L_{ss}\) is found by setting \(dL/dt = 0\),
\[
L_{ss} = \frac{U}{E} - \frac{1}{\alpha_2nF/E_F}\ln\left(\frac{k_7}{k_2^0}\right)
\]
(19)

Taking these dependencies into account, the model parameters can be optimized to match model calculation and measurements. The fitted variables are \(k_1^0, \alpha_1, k_2^0, a_2\) and \(N\). \(L\) is calculated by Equation (6) and \(k_7\) is calculated by Equation (19). The parameter \(E_F\) is guessed as \(10^6\ \text{V/cm}\).

To guarantee finding the global optimum in model parameter identification, a two-step minimization was performed based on the impedance data. For the optimization step the faradaic impedance resulting from the PDM, \(Z_{\text{PDM}}\), was summarized and the overall impedance was calculated. Using the dependencies (Equation (6), (8) and (19)) it was possible to calculate the single kinetic parameters from the overall impedance \(Z_{\text{PDM}}\). At first a genetic algorithm (in MATLAB R2015a by The MathWorks Inc) was employed to obtain initial values for the final nonlinear programming step using Matlab’s sqp solver. As constraint for the optimization it was assumed that the measured current after polarization results only from Reaction 1 and 2 \((i_{pol} = 3Fk_1C_c + 3Fk_2)\) additional to this constraint physically reasonable boundaries were used for all fitted parameters. The goodness of the fit was assessed by the \(R^2\) value.
3. Results and Discussion

3.1. Microstructure

The XRD results of the samples are shown in Figure 2. Based on the location, the α(011), α(002) and the α(211) peaks are the only visible diffraction peaks. All samples show clear martensitic diffraction pattern and no significant austenite phase. Intensity variations are among other reasons attributable to the variation in the former austenite grain size.

![Figure 2. X-ray diffraction pattern for martensitic stainless steel samples with different heat treatment.](image)

The former austenite grain size of the material increases with austenitizing temperature. It was determined using the line intersect methods of optical micrographs presented in a former study [12]. The average grain size in μm was calculated from the grain size number $G$ [33] (Figure 3). The amount of chromium carbide and the austenite content (during heat treatment) is calculated by ThermoCalc calculations (version 2018b, Table 2). It should be noted that these calculations are based on equilibrium conditions. It is assumed that 2 h of austenitizing is sufficient to dissolve all carbides and reach equilibrium (regarding the dissolution).

![Figure 3. Average grain size of martensitic stainless steel samples with different heat treatment.](image)

Cr$_2$C$_6$ carbides are dissolved at temperatures above ca. 930 °C while the Cr$_7$C$_3$ carbides completely dissolve above 1110 °C [25]. Therefore, the amount of dissolved chromium as well as the amount of dissolved carbon increases with austenitizing temperature. While a higher chromium amount leads to a more protective passive film, an increasing amount of carbon leads to lattice stress which can have a negative effect on the passive film formation [12,13,15].
Table 2. Austenite phase and mass amount of dissolved chromium.

| $T_A/°C$ | Amount of Austenite Phase (During Austenitizing) /\% | Mass Amount of Dissolved Cr /\% |
|---------|---------------------------------|-------------------------------|
| 1000    | 97.46                           | 11.94                         |
| 1050    | 98.44                           | 12.65                         |
| 1100    | 99.60                           | 13.65                         |
| 1150    | 99.97                           | 13.69                         |
| 1200    | 99.97                           | 13.69                         |

3.2. Linear Sweep Voltammetry

LSV of a selected sample was done to identify the required potential for passive film formation before each EIS measurement. The LSV measurements (Figure 4) are in agreement with literature [24]. The cathodic current peaking at ~450 mV (vs. Ag/AgCl) is a result of $H_2$ evolution, which also overlays the anodic dissolution of iron and chromium. At higher potentials, $H_2$ evolution decreases, and the dissolution of iron and chromium to $Fe^{2+}$ and $Cr^{2+}$ is accelerated. The current peak at ~300 mV is due to oxidation of chromium to $Cr^{3+}$ that leads to the formation of chromium oxide and a formation of a passive region. The passive area is characterized by a low anodic current as a result of the inhibited dissolution of chromium to $Cr(III)$ and iron to $Fe(II)$ and $Fe(III)$ for potentials over 350 mV. The transpassive area starts at a potential of 1000 mV. Here, the anodic current increases due to the oxidation of the chromium species to $Cr(VI)$ in soluble $Cr_2O_7^{2-}$, followed by $O_2$ evolution due to water electrolysis.

Figure 4. Linear Sweep Voltammetry in 0.5 M sulfuric acid; scan rate 100 mV/s.

While stationary polarization curves only show one plateau for the $Cr(VI)$ oxidation, the LSV measurements show two peaks, one at 1200 mV and one at 1500 mV.

3.3. Extraction of Kinetic Parameters from EIS Data Via the PDM

To understand the film growth kinetics as a function of austenitizing temperature the PDM parameters were fitted to the electrochemical measurements to simulate the impedance data. In a first approach, the impedance data of a test sample were fitted by the model including five interfacial reactions and the transport of anion and cation vacancies through the layer. In a second (simplified) approach, the fitting results were compared to an impedance model without consumption of cation vacancies (Reaction 1) and the cation transport through the film. This simplification, which was already done by others [30,34], seems justifiable because of two reasons. First, Reaction 1 and 2 are
two competing parallel reactions, hence either can occur without the other whereas Reaction 2 must occur for film growth. Secondly, passive films on stainless steels show n-type semiconducting behavior [35] and thus the dominant defect species are oxygen vacancies and metal interstitials (compare also MS plot in the SI). Using the first full model approach, fit results (Figure 5) and fit quality ($R^2$ value in Table 3) are slightly better compared to the simplified model. Nevertheless, also without taking the transport of defects into account, the fit quality of the reduced model is still very good. Comparison of the fitting parameter (Table 3), the standard rate constant of the film formation $k_2^0$, the rate constant of film dissolution $k_7$, and the charge transfer coefficient of the film formation reaction show very good agreement for both models.

Referring to these findings the simplified model was used to keep the set of fitting parameters as low as possible and to avoid overfitting. Hence the following admittance is used:

$$Y_F = \left( \frac{\delta I}{\delta U} \right)_{L,C} + \frac{\varepsilon \varepsilon_0}{L(\omega_m)^{N-1}} (j \omega)^N$$

The impedance data of the 6 different samples (Figure 6) reveals clear differences between the samples. The lowest overall impedance can be seen in the untreated sample (T0) (Figure 6a).

![Figure 5. Impedance data and fitting via full and reduced PDM of a test sample.](image)

| Parameter | Full Model | Simplified Model |
|-----------|------------|-----------------|
| $k_1^0$   | $2.34 \times 10^{-14}$ | –               |
| $\alpha_1$ | 0.13       | –               |
| $k_2^0$   | $7.25 \times 10^{-11}$ | $7.66 \times 10^{-11}$ |
| $\alpha_2$ | 0.028      | 0.028           |
| $k_4^0$   | $2.56 \times 10^{-14}$ | –               |
| $\alpha_4$ | 0.01       | –               |
| $k_5'$    | $2.93 \times 10^{-10}$ | $3.05 \times 10^{-10}$ |
| $E_F$     | $1.12 \times 10^6$  | $1.0 \times 10^6$ |
| $\varphi_{fs}$ | 0.1        | 0.1             |
| $D_v$     | $7 \times 10^{-16}$ | –               |
| $n$       | 0.875      | 0.875           |
| $R^2$     | 0.9974     | 0.9970          |

Up to a value of $T_A = 1100^\circ C$, the overall impedance monotonically increases with austenitizing temperature. For $T_A = 1150^\circ C$, the impedance decreases compared to the lower temperatures but a further
increase in temperature increases the impedance again, so that the maximum is reached at \( T_A = 1200\,^\circ\text{C} \) (Figure 6b).

The fitting of the impedance data can be done by the equivalent electrical (EEC) circuit presented in Figure 7. The EEC consists of an electrolyte resistance \( R_{el} \), a charge transfer resistance \( R_{ct} \), a CPE for the double layer (and the porous electrolyte filled outer layer) \( CPE_{dl} \), a CPE representing the capacitive behavior of the passive layer \( CPE_{pl} \), and an impedance element describing the interfacial reactions predicted by the PDM \( Z_{PDM} \).

The PDM calculations show good agreement with the measurements (Figure 8). The reaction coefficients for passive film growth (Reaction 2) and passive film dissolution (Reaction 7) as well as the charge transfer coefficient \( \alpha_2 \) for the film growth reaction and the passive film thickness \( L_{ss} \) are shown in Table 4.

The crucial factor for the steady state film thickness is the ratio \( \frac{k_2}{k_7} \). The higher the ratio the thicker the passive film; whereas the same ratio, which is achieved at higher rate constants, leads to the same film thickness but accelerated dissolution (for similar \( \alpha \) values) thereby approaching the steady state faster. An increasing \( \alpha \) value leads to thinning of the passive film at slightly less dissolution (assumed \( k_2 \) and \( k_7 \) remain constant).

Generally, with increasing austenitizing temperature, \( \alpha \) increases, the standard rate constant \( k_2 \) for film formation (Figure 9a) decreases, and of rate constant \( k_7 \) for film dissolution (Figure 9b)
decreases. A decrease in $k_2^0$, which means decreasing metal dissolution at the metal-passive film interface, indicates a slower corrosion rate. Thus, samples with lower $k_2^0$ show a better passivation and lower reaction rates at the metal surface due to a more protective passive layer. A further indicator for a more stable and protective passive film is the decreasing rate constant for film dissolution $k_7$. This behavior can be attributed to the higher amount of chromium at higher austenitizing temperature and a more homogeneous chromium distribution due to the higher diffusion at higher temperatures.

Figure 8. Bode plots of the impedance data of martensitic stainless steel; untreated sample (T0) and samples treated at different austenitizing temperatures recorded in 0.5 M H$_2$SO$_4$. Symbols show
experimental data whereas black lines represent the calculation using the EEC and PDM. (a) T0 untreated sample (b) 1000 °C (c) 1050 °C (d) 1100 °C (e) 1150 °C (f) 1200 °C.

| $T_A/°C$ | $k_0^/$ mol/cm²s | $\alpha_2$ | $k_5'/ $ mol/cm²s | $L_{ss}$/ nm |
|---------|-------------------|-------------|------------------|-----------|
| T0      | 9.61×10⁻¹¹         | 0.0247      | 3.60×10⁻¹⁰       | 1.50      |
| 1000    | 5.91×10⁻¹¹         | 0.0298      | 3.09×10⁻¹⁰       | 1.32      |
| 1050    | 3.68×10⁻¹¹         | 0.0282      | 1.92×10⁻¹⁰       | 1.07      |
| 1100    | 1.80×10⁻¹¹         | 0.0353      | 1.38×10⁻¹⁰       | 1.16      |
| 1150    | 2.69×10⁻¹¹         | 0.0368      | 2.66×10⁻¹⁰       | 0.76      |
| 1200    | 9.46×10⁻¹²         | 0.0352      | 8.44×10⁻¹¹       | 0.77      |

Table 4. Fitted parameters for all martensitic stainless steel samples.

Figure 9. Rate constants of film formation $k_0$ and film dissolution $k_7$ calculated by fitting the impedance data via PDM and EEC presented in Figure 8. Error bars represent standard deviations of 3 independent measurements. (a) Rate constant for film formation (b) rate constant for film dissolution.

However, the sample $T_A = 1150 °C$ shows deviations from this trend by a slightly increased rate constant for film formation and a drastically increased rate constant for film dissolution leading to the thinnest passive film. This might be connected to the dissolution of CrC₃ carbides [25], which on the one hand brings more chromium to the matrix but on the other hand leads to further lattice distortion due to the dissolved carbon. Taking the different stoichiometry of the carbides into account (Cr₂₃C₆ dissolving at 930 °C and Cr₇C₃ dissolving at 1150 °C) the ratio of dissolved carbon to dissolved chromium is higher at 1150 °C (Cr₇C₃) compared to the Cr₂₃C₆ carbides. This leads to higher lattice stress for the same amount of chromium and thus explains this behavior.

One can further observe a thinning of the passive film thins with increasing austenitizing temperature (Figure 10). The untreated sample shows the thickest passive film but also the lowest CPE parameter, $N = 0.76$, which indicates a less homogeneous layer [36]. Thus, the passive film thickness is not crucial for the protective effect of the passive layer in this case. Rather, a protective passive layer leads to a deceleration of metal dissolution at the metal–film interface and thus to a thinner but more protective film.

The simulation via the PDM shows a deviation from the impedance data for low frequencies ($10^2$ Hz). These differences could be because the model does not incorporate the transport of oxygen vacancies through the film. This vacancy transport from the metal-film interface towards the film-solution...
interface could be overcome by adding a Warburg impedance to the EEC [30] at the cost of at least one additional fitting parameter.

![Figure 10](image_url)

**Figure 10.** Passive layer characteristics obtained from impedance data analysis using the equivalent electrical circuit shown in Figure 8. (a) Passive film thickness L (Equation (6)); (b) CPE parameter N.

Fitting the passive film kinetics to the obtained impedance data provide a very good explanation for the observed dependency of corrosion resistance and austenitizing temperature [14]. Due to the higher chromium content and the more homogeneous chromium distribution the passive film is more protective and thus slows down the dissolution of the metal (decreasing rate constant for film formation) and of the film itself (decreasing rate constant for film dissolution). The results also match with our previous findings with respect to an increasing critical pitting potential [12] which indicates a slower dissolution by local corrosion attacks with increasing austenitizing temperature. Next to the increasing critical pitting potential we previously found decreasing passive current densities and decreasing corrosion rates. The fitting delivers a clear explanation for this behavior due to the decreased film formation in the passive state. Nevertheless the findings are contradictory to the findings of Candelaria et al. [13] and the decreasing start potential for pitting corrosion with increasing austenitizing temperature [12]. The presented fitting of the passive layer growth kinetics by the PDM provides detailed insight to the electrochemical behavior of the passivated samples. The phenomena investigated by Candelaria result from breakdown of passivity in the presence of halides. It is important to distinguish both mechanisms, the steady state metal loss due to growth of the passive film itself and the local corrosion attacks.

4. Conclusions

The electrochemical behavior of martensitic stainless steel was investigated with respect to the austenitizing temperature. By modeling impedance data of high reproducibility by the PDM it was possible to describe all data sets with good agreement and small standard deviations which were clearly below 10% in all cases. This agreement between calculation and data confirms that the PDM is sufficient to describe the kinetics of these passive film growths and to compare the parameters of different materials regarding their passive behavior. Furthermore, it was found that austenitizing temperature significantly influences all four kinetic parameters of passive film growth. More specifically the standard rate constant for film formation and the rate constant for film dissolution decreases with increasing austenitizing temperature. This indicates a better protection of the metal by slowing down the film growth and a more stable passive film by reducing the dissolution rate of the film itself. Both phenomena can be addressed to an increasing amount of dissolved chromium and a more homogeneous chrome distribution. This study underpins that modeling of passive film growth in combination with comprehensive electrochemical measurements has great potential for both the understanding of passivation processes and developments in materials science.
Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: Mott-Schottky plot of martensitic stainless steel sample (austenitizing temperature $T_A$: 1200 °C) after passive film formation at 600 mV for 1800 s, Figure S2 Calculated defect densities of the passive layer of martensitic stainless steel after different heat treatments.

Author Contributions: Investigation: I.B., G.M.; Writing-Original Draft Preparation, I.B.; Writing -Review and Editing, J.T., I.B.; Supervision, J.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received external funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – project number 276397488 – SFB 1232 as subproject D03 “Electrochemical High Throughput Characterization of Metallic Micro Samples”.

Acknowledgments: The authors thank Georg Pesch for proof reading of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Macdonald, D.D. Passivity—The key to our metals-based civilization. Pure Appl. Chem. 1999, 71, 951–978.
2. Ryan, M.P.; Williams, D.E.; Chater, R.J. Why stainless steel corrodes. Nature 2002, 415, 770–774.
3. Robert, T.; Foundation, A.W.; Böhni, H. Breakdown of Passivity and Localized Corrosion Processes. Langmuir 1987, 3, 924–930.
4. Soltis, J. Passivity breakdown, pit initiation and propagation of pits in metallic materials—Review. Corros. Sci. 2015, 90, 5–22.
5. McBee, C.L.; Kruger, J. Nature of passive films on iron-chromium alloys. Electrochim. Acta 1972, 17, 1337–1341.
6. Qian, S.; Newman, R.C.; Cottis, R.A.; Sieradzki, K. Computer simulation of alloy passivation and activation. Corros. Sci. 1990, 31, 621–626.
7. Qian, S.; Newman, R.C.; Cottis, R.A. Validation of a Percolation Model for Passivation of Fe-Cr Alloys: Two-Dimensional Computer Simulations. J. Electrochem. Soc. 1990, 137, 435–439.
8. Metikoš-Huković, M.; Grubač, Z.; Omanovic, S. Change of n-type to p-type conductivity of the semiconductor passive film on N-steel: Enhancement of the pitting corrosion resistance. J. Serbian Chem. Soc. 2013, 78, 2053–2067.
9. Marcelin, S.; Ter-Ovanessian, B.; Normand, B. Electronic properties of passive films from the multi-frequency Mott-Schottky and power-law coupled approach. Electrochem. Commun. 2016, 66, 62–65.
10. Guo, L.Q.; Qin, S.X.; Yang, B.J. Effect of hydrogen on semiconductive properties of passive film on ferrite and austenite phases in a duplex stainless steel. Sci. Rep. 2017, 7, 8–13.
11. Antunes, R.A.; De Oliveira, M.C.L.; Costa, I. Study of the correlation between corrosion resistance and semi-conducting properties of the passive film of AISI 316L stainless steel in physiological solution. Mater. Corros. 2012, 63, 586–592.
12. Bösing, I.; Cramer, L.; Steinbacher, M. Influence of heat treatment on the microstructure and corrosion resistance of martensitic stainless steel. AIP Adv. 2019, 9, 065317.
13. Candelaria, A.F.; Pinedo, C.E. Influence of the heat treatment on the corrosion resistance of the martensitic stainless steel type AISI 420. J. Mater. Sci. 2003, 22, 1151–1153.
14. Rosemann, P.; Kauss, N.; Müller, C.; Halle, T. Influence of solution annealing temperature and cooling medium on microstructure, hardness and corrosion resistance of martensitic stainless steel X46Cr13. Mater. Corros. 2015, 66, 1068–1076.
15. Bösing, I.; Bobrov, I.; Epp, J. Influence of Systematically Changed Martensite Content on the Passive Film Properties of Austenitic Stainless Steel in Neutral Electrolyte. Int. J. Electrochem. Sci. 2020, 15, 319–333.
16. MacDonald, D.D. Reflections on the history of electrochemical impedance spectroscopy. Electrochim. Acta 2006, 51, 1376–1388.
17. MacDonald, D.D. The history of the Point Defect Model for the passive state: A brief review of film growth aspects. Electrochim. Acta 2011, 56, 1761–1772.
18. Chao, C.Y.; Lin, L.F.; MacDonald, D.D. A Point Defect Model for Anodic Passive Films: I. Film growth kinetics. J. Electrochem. Soc. 1981, 128, 1187.
19. MacDonald, D.D. On the Existence of Our Metals-Based Civilization. J. Electrochem. Soc. 2006, 153, B213–B224.
20. Macdonald, D.D.; Urquidi-Macdonald, M. Theory of Steady-State Passive Films. *J. Electrochem. Soc.* **1990**, *137*, 2395–2402.

21. Lin, L.F.; Chao, C.Y.; Macdonald, D.D. A Point Defect Model for Anodic Passive Films: III. Impedance response. *J. Electrochem. Soc.* **1982**, *129*, 1874–1879.

22. Olsson, C.-O.A.; Hamm, D.; Landolt, D. Evaluation of Passive Film Growth Models with the Electrochemical Quartz Crystal Microbalance on PVD Deposited Cr. *J. Electrochem. Soc.* **2002**, *147*, 4093.

23. Fehlner, F.P. Low-temperature oxidation. *Philos. Mag. B Phys. Condens. Matter Stat. Mech. Electron. Opt. Magn. Prop.* **1987**, *55*, 633–636.

24. Haupt, S.; Strehblow, H.H. A combined surface analytical and electrochemical study of the formation of passive layers on Fe Cr alloys in 0.5 M H2SO4. *Corros. Sci.* **1995**, *37*, 43–54.

25. Bungardt, K.; Kunze, E.; Horn, E. Untersuchungen über den Aufbau des Systems Eisen-Chrom-Kohlenstoff. *Arch. Eisenhüttenwes.* **1958**, *29*, 193–203.

26. Yang, H.-S.; Bhadeshia, H. Austenite grain size and the martensite-start temperature. *Scr. Mater.* **2009**, *60*, 493–495.

27. Scheil, J. Entwicklung von Austenitisch—Ferritischem Gusseisen (ADI) aus EN—JS2070: Mikrostruktur, Mechanische Eigenschaften und Deren Auswirkung auf Die Oberflächenbearbeitung Durch das Maschinelle Oberflächenhämmer. Ph.D. Thesis, Technische Universität Darmstadt, Darmstadt, Germany, 2016.

28. Orazem, M.E.; Bernard, T. Kinetic Models. In *Electrochemical Impedance Spectroscopy*, 48th ed.; John Voley & Sons: Hoboken, NJ, USA, 2017; pp. 163–182.

29. Macdonald, D.; Sharifi-Asl, S.; Engelhardt, G. Review of the extraction of electrochemical kinetic data from electrochemical impedance data using genetic algorithm optimization. *Bulg. Chem. Commun.* **2017**, *49*, 53–64.

30. Sharifi-Asl, S.; Taylor, M.L.; Lu, Z. Modeling of the electrochemical impedance spectroscopic behavior of passive layers using a genetic algorithm approach. *Electrochim. Acta* **2013**, *102*, 161–173.

31. Hsu, C.H.; Mansfeld, F. Concerning the conversion of the constant phase element parameter Y0 into a capacitance. *Corrosion* **2001**, *57*, 747–748.

32. Haynes, W.M. *CRC Handbook of Chemistry and Physics*, 93rd ed.; CRC Press: Boca Raton, FL, USA, 2014.

33. ASTM Standard E112-12. Standard Test Methods for Determining Average Grain Size. *ASTM Int.* **2012**, *E112-12*, 1–27.

34. Geringer, J.; MacDonald, D.D. Modeling fretting-corrosion wear of 316L SS against poly(methyl methacrylate) with the Point Defect Model: Fundamental theory, assessment, and outlook. *Electrochim. Acta* **2012**, *79*, 17–30.

35. Schmuki, P. From Bacon to barriers: A review on the passivity of metals and alloys. *J. Solid State Electrochem.* **2002**, *6*, 145–164.

36. Bou-Saleh, Z.; Shahryari, A.; Omanovic, S. Enhancement of corrosion resistance of a biomedical grade 316LVM stainless steel by potentiodynamic cyclic polarization. *Thin Solid Film.* **2007**, *515*, 4727–4737.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).