Corrosion characteristics of a quenching and partitioning steel determined by electrochemical impedance spectroscopy

T Mehner¹,*, R Morgenstern¹, P Frint², I Scharf¹, M F-X Wagner² and T Lampke¹

¹ Materials and Surface Engineering Group, Institute of Materials Science and Engineering, Chemnitz University of Technology, 09107 Chemnitz, Germany
² Materials Science Group, Institute of Materials Science and Engineering, Chemnitz University of Technology, 09107 Chemnitz, Germany

* e-mail: thomas.mehner@mb.tu-chemnitz.de

Abstract. Among the advanced high-strength steels, quenching and partitioning (Q&P) steels provide excellent ultimate tensile strength in combination with good ductility. The mass fraction of martensite and austenite can be tailored by the Q&P treatment. In this study, the impact of the microstructure on the corrosion behaviour is investigated. For this, the microstructures of two Q&P processing routes and a quenched and tempered state are analysed using scanning electron microscopy and X-ray diffraction. Electrochemical impedance spectroscopy is conducted using two different media in order to determine the time evolution of corrosion rates during short-time corrosion. The results of this study demonstrate that correlations between Q&P microstructures and the corrosion behaviour can be analysed in detail with these experimental methods.

1. Introduction
Advanced high-strength steels (AHSS) provide excellent opportunities for light-weight design. Especially promising is the quenching and partitioning (Q&P) process, as Q&P steels combine high strength (e.g. yield stress > 1500 MPa) with a relatively large elongation to fracture > 20% [1, 2]. The Q&P process consists of austenitising at a temperature $\vartheta_a$, quenching to a temperature $\vartheta_Q$ above the martensite finish temperature directly followed by a partitioning process at $\vartheta_p$. Afterwards, the Q&P steel is cooled down to room temperature, either in air or by quenching in oil or water [3, 4]. Such processes result in microstructures that consist mainly of martensite with a small volume fraction of stabilised, interlath retained austenite. This special microstructure gives rise to interesting mechanical properties – but it potentially also leads to corrosion susceptibility. Especially low-alloy steels cannot form passive layers and, thus, are prone to (uniform) corrosion. Despite the practical importance of corrosion resistance for future applications of Q&P steels, only few related studies can be found in the literature. The corrosion behaviour of a Q&P-treated medium carbon steel in NaCl solution was investigated by Yang et al. [5] using potentiodynamic polarisation curves and electrochemical impedance spectroscopy. They found similar corrosion properties and a corrosion rate that decreased slightly for the Q&P treated steel compared to the quenched and tempered (Q&T) state of the same steel using a maximum test duration of 350 h. Lu et al. [6] studied corrosion of a stainless steel in Q&T and Q&P states in NaCl solution. Depending on the partition temperature, they found that the pitting potential was increased by about 100 mV. Thus, the Q&P treatment reduced the susceptibility to pitting when partitioned at 350 °C or 450 °C.
Further research is required concerning the short-time corrosion behaviour of low-alloy Q&P steels. Whereas the diffusion of oxygen to the surface limits the corrosion rate for neutral pH values [7], especially the regime of the acid corrosion (pH < 4), in which microstructural effects gain importance, has not yet been investigated. To address this topic, this paper focusses on corrosion-rate determination by electrochemical impedance spectroscopy (EIS) of two Q&P states of a low-alloy steel in comparison with a Q&T state of the same alloy, and on their correlation with typical microstructural features in neutral and acidic media.

2. Material and Methods
Sheets with a composition of 0.38 C, 1.92 Si, 1.39 Cr, 0.66 Mn, 0.051 S, 0.038 Mo, 0.011 P (wt%) were conventionally hot rolled to a thickness of 10 mm. Three sheets were heat-treated using the parameters summarised in table 1. They were selected in order to achieve highest strength and moderate ductility based on previous work [8].

| State | Q&T | Q&P 1 | Q&P 2 |
|-------|-----|-------|-------|
| ε austenitisation time (oven) | 950 °C, 21 min | 950 °C, 21 min | 950 °C, 21 min |
| δ0 (in water) | 60 °C | 400 °C | 350 °C |
| Molten salt temperature and holding time | – | 200 °C, 5 min | 150 °C, 5 min |
| δp and partitioning time (oven) | – | 300 °C, 10 min | 250 °C, 10 min |

Table 1. Heat-treatment parameters for the Q&T and Q&P states. The partitioning time given is the time at δp and does not include the heating time (28 min or 35 min for Q&P 1 or 2, respectively).

Specimens for EIS and scanning electron microscopy (SEM) analyses were cut from the sheets, ground and finally polished with 3 µm diamond polishing solution. The outer surface layer of about 300 µm was removed because it exhibited oxidation and decarburisation after the heat treatment. SEM was used to investigate the microstructure of the specimens. A NEON40EsB (Zeiss) microscope with a secondary-electron (SE) in-lens detector was applied with 5 kV acceleration voltage.

X-ray diffraction (XRD) measurements were performed utilising a D8 Discover diffractometer (Bruker AXS) with Co-Kα radiation (40 kV, 40 mA, point focus), a collimator with 1 mm diameter and an energy-filtered 1D Lynxeye XE detector. The diffraction diagrams were measured in the diffraction-angle (2θ) range 10°–130° with a step size of 0.01° and a time of 3.4 s/step, which corresponds to 652.8 s/step due to the use of the 1D detector. The mass fractions, the lattice parameters (a and c), microstrain (measure for the defect density, full width at half maximum (FWHM) of the Gaussian part of the line width over tan θ) and the crystallite sizes of the phases austenite and martensite were determined using the Rietveld method, considering device-related line-broadening effects.

The carbon content \( w_C \) (mass fraction in %) in the retained austenite was determined using the equation [9]

\[
w_C = \frac{a_f - 0.3573 \text{ nm}}{0.0033 \text{ nm wt%}},
\]

as a function of the lattice parameter \( a_f \) of the retained austenite.

Corrosion testing by EIS was performed in diluted H2SO4 (0.25 mol/l) or NaCl solution (0.1 mol/l, pH 7) at 25 °C utilising an electrochemical work station IM6 (Zahner Elektrik GmbH) using a three-electrode setup with Ag/AgCl-saturated KCl reference electrode and a corroded area \( A \) of 0.785 cm². For all specimens, 30 consecutive measurement cycles were performed, each one consisting of

- open circuit potential (OCP) stabilisation for 10 min,
- EIS measurement (amplitude 2 mV, 4 kHz–45 mHz, 5 frequencies per decade and 20 repetitions per frequency) for 23 min.
Thus, the total measurement time was 16.5 h per specimen. At least 4 specimens of each state were studied. The 30 EIS spectra for each specimen were interpolated linearly in time in order to extract spectra between 1.5 h and 14.5 h with a step size of 0.5 h. These spectra were averaged for each heat-treatment state. The equivalent circuit used for evaluation is shown in figure 1. It consists of a solution resistance $R_s$, charge-transfer resistance $R_{ct}$ and an imperfect capacitor, a so-called constant-phase element (CPE). $R_{ct}$ and the CPE represent the electrochemical behaviour of the specimen. The imperfection of the capacitor results mainly from the diffuse double layer and the surface roughness of the specimen.

![Figure 1. Equivalent circuit used for EIS.](image)

The corrosion rate $k_{corr}$ is inversely proportional to $R_{ct}$. For Fe, it can be calculated by [10]:

$$k_{corr} = 0.9987 \frac{\text{mm} \cdot \text{cm}^2 \cdot \text{Ω}^{-1}}{\text{a} \cdot \text{K} \cdot \text{A} \cdot R_{ct}}$$ in H$_2$SO$_4$ and

$$k_{corr} = 0.9248 \frac{\text{mm} \cdot \text{cm}^2 \cdot \text{Ω}^{-1}}{\text{a} \cdot \text{K} \cdot \text{A} \cdot R_{ct}}$$ in NaCl, (3)

with the absolute temperature $T$.

![Figure 2. SEM micrographs of Q&T (a), Q&P 1 (b) and Q&P 2 (c). The red circles indicate examples of carbides and the arrows highlight retained austenite.](image)
3. Results and discussion

3.1. Microstructural characterisation

Typical SEM micrographs of the three different heat-treated states are shown in figure 2. Clear evidence of carbides in the Q&T martensitic areas can be found (see figure 2 (a)). Minor fractions of carbides rarely occur in the Q&P states as well (see figures 2 (b) and (c)). The microstructures of both Q&P processed conditions show similar features. Even though retained austenite and martensite cannot easily be distinguished microscopically, the Q&P states exhibit more areas in which austenite is likely present. Yang et al. found the retained austenite as interlath phase between the martensite laths in Q&P treated samples and almost no traces of inter-lath austenite in Q&T states [5]. A similar distribution can be assumed here. A quantification of the phase fractions was done by XRD. The diffraction diagrams revealed the presence of martensite and austenite only, whereas no carbide phases were detected. Thus, the mass fraction of these additional phases is below 1 %. Table 2 summarises the parameters determined by XRD and $w_C$ for the three states ($a, c$ – lattice parameters of martensite).

| Table 2. Parameters of the phases martensite and austenite. |
|-------------------------------------------------------------|
|                | Q&T | Q&P 1 | Q&P 2 |
|----------------|-----|-------|-------|
| **Martensite**  |     |       |       |
| Mass fraction (%) | 97.5| 92.5  | 92.0  |
| $a$ (nm)        | 0.2881| 0.2882| 0.2873|
| $c$ (nm)        | 0.2856| 0.2857| 0.2851|
| Crystallite size (nm) | 57 ± 1| 50 ± 1| 66 ± 2|
| Microstrain ($^\circ$) | 0.793| 0.766 | 0.560 |
| **Austenite**   |     |       |       |
| Mass fraction (%) | 2.5 | 7.5   | 8.0   |
| $a_\gamma$ (nm) | 0.3600| 0.3606| 0.3611|
| Crystallite size (nm) | 17 ± 3| 30 ± 3| 37 ± 10|
| $w_C$ (%)       | 0.82 | 1.00  | 1.15  |

The Q&T state still contains a typical, small fraction of retained austenite, which is probably a consequence of stabilising effects of mechanical stresses and C diffusion during the cool-down processes. The two Q&P states possess almost the same amount of retained austenite (7.5–8.0 %), but show significant differences in terms of the other microstructural parameters: Q&P 2 has smaller lattice parameters, a larger crystallite size for martensite and larger $w_C$ in austenite. Due to the longer total time for partitioning and heating up, the recovery processes in the martensite phase can take place more intensely and thus reduce microstrains while also increasing the crystallite size. The lower quenching and holding temperature likely results in an even lower solubility of C in the martensite compared to Q&P 1, increasing the C diffusion rate into the austenite. As a consequence, $w_C$ is larger for Q&P 2. The similarity between the microstructural parameters of the martensite phases of Q&T and Q&P 1 is remarkable: As the lattice parameters of martensite are almost identical but the retained austenite contains more carbon for Q&P 1, the presence of carbide phases in Q&T is evident, which can be observed in the microstructural images in figure 2.

3.2. EIS characterisation

In figure 3, typical Nyquist plots of EIS measurements of the three heat-treatment states in H$_2$SO$_4$ are shown. Clear differences between Q&T and Q&P can be identified. The diameter of the semicircle is significantly larger for Q&T compared with Q&P, indicating a lower corrosion rate for Q&T. The calculated $R_{ct}$ values for corrosion in both H$_2$SO$_4$ and NaCl were converted into corrosion rates (equations (2) and (3)), which are shown in figure 4 as a function of corrosion time. The corrosion appearance was uniform in both media.
Figure 3. Exemplary Nyquist plots (impedance $Z$) measured during the corrosion of the three heat-treatment states in H$_2$SO$_4$ after 10 h.

Figure 4. Time dependence of the corrosion rates of Q&T and Q&P heat-treatment states for the corrosion in NaCl (a) and H$_2$SO$_4$ (b). The numbers given are time averages of the corrosion rates.

For NaCl, all corrosion rates show a minimum after 4 h. This is a consequence of the formation of a passive layer due to the initial corrosion, which reduces the corrosion rate by about 10%. The passive layer is dissolved in the further corrosion process leading to an increase of the corrosion rate, which reaches the initial value after about 8 h. After a corrosion time of about 12 h, the corrosion rate appears to stabilise. The differences between Q&P 1 and Q&P 2 are almost negligible. Another study with a low time resolution indicates an almost constant corrosion rate up to about 30 h, which is in agreement with the results in figure 4, followed by a significant increase [5]. For neutral pH values (7 for the NaCl solution), the differences of the microstructure (e.g. crystallite size or defect density) do not lead to differences of the corrosion rate, as the diffusion of oxygen to the surface limits the velocity of the cathode reaction and thus the corrosion rate [7]. However, significant differences of the phase composition can increase the corrosion velocity e.g. by increasing the cathodic area fraction. As the cathodic reaction is the reaction-rate limiting process for Fe [11], this will increase the corrosion rate: C atoms solved in martensite alter the potential of the areas to be more cathodic [12]. Figure 5 schematically shows the difference of the C distribution that may lead to an increase of the cathodic area for the Q&T state compared with Q&P: In Q&T, the C atoms are primarily solved in the martensite phase (only 2.5% of retained austenite, black in figure 5 (a)). In proximity to the retained austenite, the C content in martensite drops because the C atoms can diffuse into the retained austenite during the tempering process (light grey areas). Due to the different concentration of C atoms, the martensitic areas close to the retained austenite will be more anodic compared to the other parts of the grain (dark grey...
areas). Thus, the grains mostly form cathodic areas with anodic parts near the retained austenite. The retained austenite is also cathodic to the martensite [13] in this medium. In Q&P (figure 5 (b)), in contrast, the C content and its difference within different parts of the martensitic grains is low and thus the differences between martensite and austenite predominantly determine the corrosion behaviour in neutral NaCl solution. The total cathodic area (retained austenite) in the Q&P state is smaller than in the Q&T state (C-rich martensite and retained austenite). Comparing Q&T with Q&P heat treated materials, this model rationalises the 10 % increase of the corrosion rate in Q&T.

![Figure 5](image-url)

**Figure 5.** Schematic representation of the microstructure in Q&T (a) and Q&P (b) states. Black lines correspond to austenite and grey areas to martensite. In dark grey, cathodic C-rich martensite areas are shown.

The low pH value in the H$_2$SO$_4$ solution allows for hydrogen formation as the cathodic reaction and thus significantly increases the corrosion rate compared with the NaCl solution. In diluted H$_2$SO$_4$, the corrosion rates of the Q&P states are about a factor of 2 higher compared to that of the Q&T state. The dual-phase microstructure of the Q&P specimens can form a microscopic galvanic (bimetallic) corrosion element enhancing the velocity of the corrosion reaction. The highly-dispersed distribution of the austenite phase in the Q&P states results in the formation of a large number of such galvanic corrosion elements and thus in a significant increase of the corrosion rate compared with Q&T. The larger amount of carbon in the retained austenite in Q&P 2 reduces the hydrogen overpotential [12] leading to a further increase of the corrosion rate in comparison with Q&P 1. This also means that carbon atoms diffuse to defect sites (e.g. dislocations) in the retained austenite, forming additional corrosion elements and spots with reduced hydrogen overpotential, which both lead to a local favour of the cathodic reaction. With progressing time, the corrosion rate strongly increases (by almost a factor of 2), which is most likely related to the increase of the surface roughness and thus the size of the reactive area. This larger area provides even more cathodic areas and, in consequence, increases the corrosion rate.

4. Summary and conclusions

Depending on the corrosion system, Q&P treatments can improve or lower the corrosion resistance compared to a Q&T state of the same alloy. For neutral pH values with Cl$^-$ ions, the Q&P specimens show lower corrosion rates compared with Q&T specimens. During the corrosion in NaCl solution, a short-time passivation (< 4 h) of all specimens occurs. The stability of this layer is low and thus it quickly dissolves. The general time evolution of the three states is similar. In diluted H$_2$SO$_4$, the average corrosion rate of the Q&P states is significantly higher (65 % for Q&P 1 and 80 % Q&P 2) than for the Q&T treatment at any time. In addition, within the first 16 h, it nearly doubles for the Q&P states. This increase is nearly linear in time with a slightly decreasing slope. Even though the state Q&P 1 shows a 10 % lower corrosion rate compared with Q&P 2, the overall very high corrosion damage of this steel in any heat-treatment condition in the acid medium proves the necessity for a corrosion protection in such aggressive environments. In the light of recent advances and potential applications of Q&P steels, there is a need for further, in-depths studies on the corrosion behaviour –
both on elementary corrosion mechanisms in multi-phase microstructures, and on engineering solutions to provide better corrosion protection to this promising class of structural materials.

5. References

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