Improvement of the martensitic stainless steel X46Cr13 by Q&P heat treatment

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Abstract. The innovative heat treatment concept of "Quenching and Partitioning" (Q&P) enables the production of high-strength martensitic steels with high ductility. Residual austenite is stabilized in the partitioning process by carbon diffusion. This enables the strain-induced phase transformation from austenite to martensite and increases the ductility without reducing the strength. So far, little research has been done on the application of the Q&P process on martensitic stainless steels and their related corrosion resistance. The present work supplements the first investigations by Yang and Raabe with important material-technical parameters as well as the achievable corrosion resistance. The Q&P heat treatment offers enhanced mechanical properties and a higher corrosion resistance in comparison to the conventional quenching and tempering heat treatment.

1 Introduction

The usability of all products depends on the properties of the used materials. Whenever a further development of technical applications exceeds the application limits of the materials used, an alternative material concept is required. For example, the increase in efficiency of aircraft engines due to the increase in the combustion temperature necessitates a substitution of the nickel-based alloys currently used as a turbine material [1]. However, new developments are not always necessary. The targeted optimization of the properties of existing material concepts is often sufficient, which can be ensured by adapting the manufacturing parameters and the applied heat treatment.

The so-called "Quenching and Partitioning" (Q&P) is a new heat treatment concept for high-strength steels with increased ductility [2, 3]. Figure 1 presents the Q&P heat treatment process. The first step is the austenitization which aims on the homogenous distribution of alloying elements within the austenite. The subsequent quenching is stopped at a specific temperature between the martensite start (Ms) and finish temperature (Mf) to target a defined proportion of retained austenite (RA) in the martensite. The final partitioning at low tempering temperatures induces carbon diffusion from martensite into the RA, which is favoured due to the higher carbon solubility of the face-centred cubic crystal structure [4, 5]. This carbon enrichment further reduces the Ms temperature and stabilizes the RA [6]. A special feature of this stabilized RA is the property of transforming strain-induced into martensite under mechanical load. The effect, referred to as TRIP (transformation induced plasticity), increases strength and deformability of the steel [7, 8]. While previous studies on the Q&P process mostly focus on low-alloy steels, there are current studies on corrosion-resistant, martensitic steels like X46Cr13. Q&P heat treatment offers several advantages for this type of steel. On the one hand, the heat treatment process is
simplified because $M_f$ is below room temperature (RT) [9]. This eliminates the need for interrupted quenching in the first part of the Q&P process, which is necessary for low-alloy steels. On the other hand, with optimal heat treatment parameters, very high strengths ($\sim$ 1,800 MPa) with good elongation at fracture (20 %) can be achieved [11] and may be combined with high corrosion resistance.

**Figure 1.** Temperature-time curve and structural change in Q&P heat treatment [10].

Furthermore, carbon accumulation occurs at large and small angle grain boundaries of the martensite. This enables the local transformation of martensite back into so-called "reverted" austenite (revA) [11], see Figure 2.

**Figure 2.** a) Diffusion of carbon during partitioning (red arrows), b) resulting microstructure (martensite = white; stabilized austenite = red) [9].

Due to the high chromium content, finely disperse carbides are formed during partitioning, which further increase the strength by particle hardening [9, 10]. The present work is intended to contribute to the characterization of the property profile (structure, strength, deformability and corrosion resistance) of the stainless steel X46Cr13 depending on the duration of the partitioning.
2 Material and methods
The used material was the martensitic stainless steel X46Cr13 (1.4034, AISI 420). The chemical composition of the cold-rolled and then soft annealed initial state is given in Table 1.

Table 1. Chemical composition of the martensitic stainless steel X46Cr13 in wt.-%.

| Element | Fe  | C    | Cr   | Mn  | Si  | Ni  | Mo  | N   | P   | S   |
|---------|-----|------|------|-----|-----|-----|-----|-----|-----|-----|
| Content | bal. | 0.45 | 13.95 | 0.65 | 0.34 | 0.12 | 0.02 | 0.02 | 0.012 | <0.001 |

The selection of heat treatment is based on the studies by Yuan [11], but were partially adjusted. The samples were austenitized for 15 min at 1150 °C in order to dissolve large carbides (≈ 10 μm) from the soft annealed initial state. The samples were quenched to room temperature in water after austenitization. The partitioning was carried out at 400 °C (T_p) and the partitioning time (t_p) was varied in order to investigate the time-dependent phase formation of revA and its influence on the properties. Three main states were created:

- not partitioned quenched reference condition
- 5 min partitioned short-term partitioning
- 30 min partitioned long-term partitioning

The mechanical behavior was determined by tensile and compression tests (according to DIN 50125 and DIN 50106). The phases in the microstructure were quantified by X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) with a scan step size of 100 nm. Furthermore, the structure was visualized using optical microscopy (OM). For these investigations, the samples were first ground and polished. The XRD analysis was carried out on sample surfaces additionally etched with V2A. For the EBSD examinations, the samples were polished with OPS to completely remove preparation-related surface deformation. The light microscopic evaluation was carried out on Beraha II etched surfaces.

The corrosion resistance of the stainless steel X46Cr13 is also significantly influenced by the heat treatment [12]. To demonstrate the advantages of Q&P heat treatment compared to conventional hardening and tempering, electrochemical potentiodynamic reactivation (EPR) and the KorroPad test were used. The EPR method allows to characterize the passivation and reactivation behavior of the different heat treatment conditions [12]. A 0.1 M H_2SO_4 solution and a classic three-electrode arrangement, consisting of working electrode (sample), Ag/AgCl reference electrode (+198 mV NHE) and platinum counter electrode, were used. The sample was polarized with 2 mV/s from -500 mV to +100 mV_{Ag/AgCl} to form the passive layer (passivation). The direction of polarization was reversed at +100 mV_{Ag/AgCl} and polarized back to -500 mV_{Ag/AgCl} (reactivation) in order to induce the dissolution of chromium-depleted zones. The influence of the heat treatment on the pitting corrosion resistance was examined with the KorroPad test [13, 14]. This enables very quick detection of corrosion-prone microstructure conditions on martensitic stainless steels [15, 16]. All samples were ground with 180 grit SiC paper and then passivated for 24 h at more than 95 % relative humidity to form a stable passive layer. The KorroPads with 0.1 M NaCl and 1 mM K_2[Fe(CN)_6] were applied on the passivated surface for 15 min and compared visually. Blue color indications are the result of pronounced pitting corrosion.

3 Results and discussion
3.1 Mechanical properties
The influence of the partitioning time on the mechanical properties of the martensitic stainless steel X46Cr13 is shown in Figure 3. The quenched reference state exhibits brittle fracture during the tensile tests before the yield strength is reached. This behavior is typical for brittle materials, which include...
X46Cr13 in the hardened state. Even with a partitioning time of 5 minutes, an enormous increase in strength and elongation can be seen, while the fracture occurs in the plastic deformation area. By increasing the partitioning time to 30 min, the deformability is furthermore increased. A tensile strength of nearly 1,700 MPa and a total elongation of 12 % are achieved. It should be noted that a deviating behavior in the elastic range was detected for the partitioned states, which contradicts the literature [17] and is attributed to the experimental setup.

Figure 3. Results of the mechanical testing: a) tensile and compression test, b) tensile test.

In contrast to the tensile tests, the compression tests show identical behavior for all states. No statement can be made about the maximum strength and the maximum deformability, since the tests had to be stopped when the load limit of the testing machine was reached, while no sample failure occurred. However, it can be seen that yield point, maximum strength and deformability exceed the characteristic values of the tensile tests. Based on the assumption that plastic deformation is only caused by shear stresses, the compressive and tensile strengths of materials should be identical [18].

However, this is not the case with high-strength steels and especially with martensite. It has been proven experimentally that high-strength steels can withstand higher pressure loads. This behavior is referred to the SD (strength differential effect) [19, 20]. The causes of the different mechanical parameters have not yet been fully clarified. It is assumed that several influencing factors are involved, but there is no consensus on the specific contribution.

Accordingly, it is conceivable that microcracking limits the deformability under tensile load. Other possible influencing factors are the Bauschinger effect, interactions between dislocations and interstitially embedded atoms, and the residual stresses that depend on the direction of mechanical load [19–21]. For the steel 100Cr6, Ellermann and Scholtes have determined, that the conversion of residual austenite to martensite by the TRIP effect is suppressed under pressure loads [21].

This last aspect in particular would explain the higher deformability of the partly austenitic samples. In addition, the SD effect in martensitic steels, of a maximum of 10 %, cannot be explained with the results of the present work. SINGH et al. also report that the SD effect decreases with increasing tempering temperature [19]. Further investigations are required to explain the different mechanical behavior of Q&P heat treatment under tensile and compressive loads.

Figure 4 presents the fractured surface of the tensile specimens imaged by SEM. The proportion of ductile fracture increases with the partitioning time, which can be seen from the typical honeycomb structure. This observation is in line with the increase in the total elongation in the tensile test with increased partitioning time (Figure 3). Furthermore, all samples show a terrace-shaped fracture surface and the crack growth is preferably transverse to the tensile direction. The cause of this behavior is determined by the microstructure analysis in section 3.2. in more detail.
3.2 Phase and microstructure analysis

The influence of the Q&P heat treatment on the phase components was determined by X-ray analysis and the corresponding results are presented in Figure 5. The quenched state consists mainly of strongly distorted α-Fe (martensite), which can be seen from the broad α-Fe peak which is shifted slightly relative to the reference position. In addition, large fractions of austenite were detected.

The width of the α-Fe peak decreases with increasing partitioning time, which is related to the decrease of residual stresses in the martensite. This is caused by the diffusion-related decrease of the carbon content in the martensite. The peak intensity of the austenitic fcc phase increases with longer partitioning. The cause is the time-dependent austenite reversion due to the partitioning, which increases the austenite content. The results of EBSD presented in Figure 6 confirm the XRD results. The structure of the quenched state consists of martensite and islands of residual austenite.
Figure 6. EBSD images after Q&P heat treatment (martensite/bcc: red; austenite/fcc: blue).

5 min partitioning exhibits more dispersed austenite areas between the martensite. These phases grow with increasing partitioning time, which can be seen at 30 min partitioning time. Reverted austenite forms at the sub-grain boundaries of martensite. According to YUAN et al. the reverted austenite also forms like a film at the boundaries of the primary austenite grains [11]. However, this only has an extent of a few nanometers and cannot be detected by EBSD. For additional evaluation, OM images of the microstructures are finally presented in Figure 7. A pronounced line like structure was detected for all states, which partially extends over the entire cross-section of the sample.

Figure 7. OM after Q&P heat treatment etched with Beraha II (martensite: black, austenite: white).

The white lines are primary austenite and the comparison with the images of the terraced fracture surfaces in Figure 4 suggests that the crack propagation takes place preferentially in the austenitic lines. SEM images in BSE contrast in combination with EDX analyses also show that there is a further phase within the austenite lines, see Figure 8. EDX analyses show that these are chromium-rich carbides within the austenitic lines. Their poor deformation properties cause the preferred crack growth during tensile load along the carbides. The large carbides are already contained in the soft-annealed starting material and thus originate from the hot- and cold-rolling during sheet metal production. These are the result of too low rolling temperatures, which lead to the formation of carbide lines along the grain boundaries of the stretched grains. The subsequent soft annealing leads to further growth of this carbides and cause the formation of large carbide agglomerations.
These agglomerates were not completely dissolved by austenitizing at 1150 °C for 15 min in the first step of Q&P heat treatment. Obviously, the homogeneous distribution of all alloy elements within the austenitic matrix was not achieved. The partly dissolved carbides result in a local enrichment of the surrounding matrix with C and Cr. The residual austenite preferably remains around the carbides due to the locally decreased M_f temperature.

3.3 Electrochemical investigations of the corrosion resistance

Figure 9 shows the results of the electrochemical potentiodynamic reactivation as a direct comparison of tempering (a) with Q&P heat treatment (b). Conventional hardening at 1050 °C for 15 min followed by water quenching achieves a corrosion-resistant state, since chromium is homogeneously distributed in the martensitic matrix, although a large number of carbides are still present in the structure. Conventional tempering results in the formation of sub-microscopic, chromium-rich carbides and induce chromium depletion at a low tempering temperature of 400 °C. This can be seen from the increased passivation and reactivation current densities.

If the tempering temperature is increased to the usually used tempering temperature of 600 °C, the passivation behavior is severely disturbed, since the matrix is strongly depleted by progressive carbide...
formation and carbide growth. This condition is no longer able to form a stable passive layer and exhibits a detrimental corrosion resistance.

In contrast, the Q&P heat treatment, even after partitioning at 400 °C for 30 min, no chromium depletion can be detected using the EPR method and a stable passive layer is formed in all conditions. This is due to the lower temperature and shorter duration during partitioning which avoid carbide formation and chromium depletion. The differences in passive layer stability demonstrated with the EPR method have a very strong influence on the pitting corrosion resistance. This is illustrated by the results of the KorroPad test in Figure 10.

Figure 10. Results of the KorroPad test as a comparison of remuneration and Q&P.

Conventional hardening results in high pitting corrosion resistance, but tempering at 400 °C and 600 °C causes a strong susceptibility to pitting corrosion, which can be seen from the large blue indications that appear when individual pits grow during the KorroPad test. The portioned states, on the other hand, have a high pitting corrosion resistance. From a corrosion point of view, Q&P heat treatment has clear advantages compared conventional tempering.

4 Conclusions
The Q&P heat treatment was tested on the martensitic stainless steel X46Cr13. The focus of the investigations was the influence of the partitioning on mechanical properties, microstructure and corrosion resistance. The following findings were achieved:

1. The quenched state suffers from brittle fracture before the yield strength is reached. A tensile strength of ≈ 1.700 MPa and a total elongation of ≈ 12 % were achieved by partitioning up to 30 min and a pronounced SD effect was detected.

2. The improvement of the mechanical properties is based on the mechanisms of austenite stabilization and reversion. Both are the consequence of time-dependent diffusion of carbon during partitioning.

3. The corrosion resistance after Q&P heat treatment is significantly higher in comparison to the conventional tempered condition, since the diffusion-induced formation of austenite does not cause chromium depletion during partitioning.

Furthermore, it was found that austenitizing (1150 °C, 15 min) must be classified as insufficient, since the large, chromium-rich carbides of the soft-annealed initial state were not dissolved. Consequently, there are line areas of residual austenite around remaining carbides within the microstructure. The carbon diffusion during partitioning does not completely stabilize them. It is assumed that optimization of the soft annealing initial microstructure may further increase the tensile strength and total elongation. This requires the loosening of all carbides and a homogeneous distribution of the alloy elements during austenitizing as an optimized starting point for partitioning.
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