CORROSION AND FATIGUE OF HEAT TREATED MARTENSITIC STAINLESS STEEL 1.4542 USED FOR GEOTHERMAL APPLICATIONS

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Abstract

During capture and storage technology (CCS) as well as in geothermal energy production steels need to withstand the corrosive environment such as: heat, pressure, salinity of the aquifer and CO₂-partial pressure. 1.4542 shows unusual corrosion phenomena, but is still sufficiently resistant in corrosive environments. To better understand its behaviour differently heat treated coupons of 1.4542 and for comparison X20Cr13 and X46Cr13 were kept in the artificial brine of the Northern German Basin at T=60 °C. Ambient pressure as well as p=100 bar for 700 h - 8000 h in water saturated supercritical CO₂ and CO₂-saturated synthetic aquifer environment was applied. Fatigue tests were performed via push-pull tests with a series of 30 specimens from 150 MPa to 500 MPa (sinusoidal dynamic test loads, R=-1; resonant frequency ~ 30 Hz). FeCO₃ and FeOOH are corrosion products also after dynamic corrosion tests. Martensitic microstructure offers good corrosion resistance in geothermal environment. The S-N-curve showing no typical fatigue strength and very steep slopes of possible fatigue strength for finite life. Possible influencing artefacts, such as Al-inclusions could not be correlated to early rupture
Despite specimens containing inclusions at the fracture surface and cross section reached lower number of cycles. Applied potential proofed to enhance fatigue life tremendously.

**Keywords**

High Alloayed Steel, Pitting; Corrosion Fatigue, Corrosion, Endurance Limit, CCS, CO₂-Storage

### 1. Introduction

Emission gases e.g. from combustion processes of power plants are compressed into deep geological saline aquifers CCS-site (CCS Carbon Capture and Storage (Thomas, 2005; van den Broek, Hoefnagels, Rubin, Turkenburg, Faaïj, 2010)) will result in corrosion of piping and casing of the CCS engineering site (Nešić, 2007; Hurter, 2008; Zhang, Yang, Sun, Lu, 2008; Mu and Zhao, 2009; Seiersten, 2001; Cui, Wu, Uhu, Yang, 2006; Pfennig and Kranzmann, 2011). Injection pipe steels are highly sensitive towards CO₂-corrosion regarding alloy composition, contamination of alloy and media, temperature, CO₂ partial pressure, flow conditions and protective passivating corrosion scales (Zhang, Yang, Sun, Lu, 2008; Mu and Zhao, 2009; Zhang, Zhao, Juang, 2005; Alhajji and Reda, 1993; Choi and Nešić, 2008; Jiang, Nešić, Huet, 2008; Ahmand, Allam, Abdul Aleem, 2000; Pfennig and Bääbler, 2009; Pfennig and Kranzmann, 2010; Pfennig, Zastrow, Kranzmann, 2013; Nybor, 2005; Carvalho, Joia, Mattos, 2005; Linter and Burstein, 1999; Wu, Cui, Zhao, Yan, Zhu, Yang, 2004).

Alloying elements (Bülbul and Sun, 2010) and heat treatment (duration, temperature of initial austenitizing and annealing as well as cooling rate (Hou, Li, Li, Zhang, 2000; Cijovic and Radenkovic, 2006; Park and Park, 2007)) significantly influence the corrosion behaviour of steels. In general Ni- and Cr contents (Banaš, Lelek-Borkowska, Mazurkiewicz, Solarski, 2007; Bilmes, Llorente, Méndez, Gervasi, 2009) improve the corrosion resistance. Retained austenite improves pitting corrosion resistance (Banaš et al., 2007). Higher austenitizing temperature for martensitic steels (Zhang et al., 2001; Brown, Parakala, Nešić 2004; Isfahany, Saghafian, Borhani, 2011) and annealing at higher temperature of lean duplex stainless steels (Bülbul and Sun, 2010; Hou et al., 2000; Zhang et al., 2001) decrease the susceptibility towards local corrosion. NaCl solution containing H₂S severely degrades Mn-containing carbon steels with martensitic microstructure compared to ferritic or ferritic-bainitic microstructures (Lucio-Garcia et al., 2009) due to reactive grain boundaries in martensitic microstructures.

Locally corroded samples -with pits acting as corrosion catalyzer- usually reveal similar corrosion products as the slowly growing surface layers (Pfennig and Bääbler, 2009; Pfennig et
al., 2013). Generally siderite FeCO$_3$ (Nešić, 2007; Han, Yang, Nešić, 2008; Pfennig, Wolthusen, Zastrow, Kranzmann, 2015) precipitates on steels in contact with CO$_2$-environment because the solubility of FeCO$_3$ in water is low ($p_{K_{sp}} = 10.54$ at 25 °C (Brown et al., 2004; Han et al. 2008)) and consequently anodic iron dissolution takes place. Transient Fe(OH)$_2$ is formed initially (Mu and Zhao, 2009; Isfahany et al., 2011) which may locally increase the pH in proximity to the hydroxide film followed by the consecutive formation an internal and external ferrous carbonate (Han et al., 2008) according to equations 1 to 6 (Pfennig and Bäßler, 2011; Brown et al., 2004):

\[
\text{CO}_2 (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}^+ + \text{HCO}_3^- (aq) \quad (1)
\]

\[
\text{cathodic:} \quad 2 \text{HCO}_3^- + 2 \text{e}^- \rightarrow 2 \text{CO}_3^{2-} + \text{H}_2 \quad (2)
\]

\[
\text{anodic:} \quad \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (3)
\]

\[
\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3 \quad (4)
\]

\[
\text{Fe}^{2+} + 2 \text{HCO}_3^- \rightarrow \text{Fe(HCO}_3)_2 \quad (5)
\]

\[
\text{Fe(HCO}_3)_2 \rightarrow \text{FeCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (6)
\]

Corrosion layers and pitting have been reported to cause early failure of materials under cyclic load (Madduri and Prakash, 2010; Msahiro, 1999; Vignal, Delrue Peultier, Oltra, 2007). Local corrosion on stainless steels is enhanced by

- Chemical corrosion reactions,
- Changes of lattice energy locally within the steel`s surface and

Cracks are initiated and crack propagation is enhanced and accelerated at dual or triple points of grain/phase boundaries where the grain/phase boundary energy is higher (Madduri and Prakash, 2010; Vignal et al., 2007). The local lattice mismatch at grain/phase boundaries also initiates pit formation, selective corrosion and inter granular deterioration resulting crack formation (Masahiro, 1999).

Parts of this work have been presented at GHGT13 (Pfennig et al., 2015), ICFEE 2017 (Pfennig and Kranzmann, 2017) and ICBEE 2019 (to be published) and we will now give an update on new findings, summarize all our previous work of the last 10 year and compare results to heat treated martensitic stainless steels (1.4022 and 1.4043). This is our final review work on corrosion kinetics of X20Cr13, X46Cr13 and X5CrNiCuNb16-4. Further investigation will comprise the corrosion mechanism, respectively.
2. Materials and Methods

Both, immersion tests as well as corrosion fatigue tests were undertaken for the same steel quality (martensitic AISI 630, X5CrNiCuNb16-4, 1.4542, tensile strength in air: 1078 MPa) (Table 1) using synthesized Stuttgart Aquifer (Förster et al., 2006): Ca$^{2+}$: 1760 mg/L, K$^{2+}$: 430 mg/L, Mg$^{2+}$: 1270 mg/L, Na$^{2+}$: 90,100 mg/L, Cl$^{-}$: 143,300 mg/L, SO$_4^{2-}$: 3600 mg/L, HCO$_3^{-}$: 40 mg/L). For fatigue tests the surfaces were activated via machining to Rz=4.

**Table 1: Element distribution of 1.4542 (X5CrNiCuNb16-4, AISI 630), (mass percent)**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>acc</td>
<td>≤ 0.07</td>
<td>≤ 0.70</td>
<td>≤ 1.50</td>
<td>≤ 0.04</td>
<td>≤ 0.015</td>
<td>15.0 - 17.0</td>
<td>≤ 0.60</td>
<td>3.00 - 5.00</td>
<td>3.00 - 5.00</td>
<td>0.20 - 0.45</td>
</tr>
<tr>
<td>standard a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>analysed b</td>
<td>0.03</td>
<td>0.42</td>
<td>0.68</td>
<td>0.018</td>
<td>0.002</td>
<td>15.75</td>
<td>0.11</td>
<td>4.54</td>
<td>3.00</td>
<td>0.242</td>
</tr>
</tbody>
</table>

- a) elements in accordance to DIN EN 10088-3 in %
- b) measured via spark emission spectrometry

Heat treatment (Table 2), sample preparation, laboratory scale exposure tests using coupons (8 mm thickness, 20 mm width, 50 mm length) and corrosion fatigue tests as well as electrochemical in-situ and optical analysis procedures have been widely described in detail in our previous work (Pfennig and Bäßler, 2009; Wolf, Afanasiev, Böllinghaus, Pfennig, 2016; Pfennig and Kranzmann, 2017, Pfennig, Heynert, Wolf, Böllinghaus, 2014)

**Table 2: Heat Treatment Protocol for X5CrNiCuNb16-4**

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Temperature</th>
<th>Time in min</th>
<th>Cooling Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>normalizing</td>
<td>850°C / 850°C</td>
<td>30</td>
<td>oil</td>
</tr>
<tr>
<td>hardening</td>
<td>1040°C</td>
<td>30</td>
<td>oil</td>
</tr>
<tr>
<td>hardening and tempering 1, 550 °C</td>
<td>1040°C / 550°C</td>
<td>30</td>
<td>oil</td>
</tr>
<tr>
<td>hardening and tempering 2, 650 °C</td>
<td>1040°C / 650°C</td>
<td>30</td>
<td>oil</td>
</tr>
<tr>
<td>hardening and tempering 3, 755 °C</td>
<td>1040°C / 755°C</td>
<td>30</td>
<td>oil</td>
</tr>
</tbody>
</table>

Temperature, pH and electrochemical potential were measured directly within the corrosion chamber using an Ag/AgCl wire electrode fixed in a Teflon channel to measure the open-circuit electrochemical potential. Fatigue tests were carried out at 30 – 40 Hz in stress-strain mode under CCS aquifer environment with additional technical CO$_2$ (flow rate. 9 L/h). Temperature fluctuation was kept below ± 0.3 K and mean frequency of the cyclic load accounted to 30-33 Hz.
3. Results and Discussion

According to DIN 6601 the following equation was used to calculate surface corrosion rates:

\[ \text{Corrosion rate: } \omega = \frac{8760 \left[ \frac{mm}{year} \right] \times 10 \left[ \frac{mm}{cm} \right] \times \text{weight loss}[g]}{area[cm^2] \times \text{density} \left[ \frac{g}{cm^3} \right] \times \text{time}[hour]} \] (7)

Corrosion rates obtained after exposure to the liquid phase are much higher (by a factor of 3 after 8000 h of exposure) indicating the different reaction kinetics in different atmospheres. Diffusion in the liquid phase is slower prohibiting the precipitation of a continuous passivating corrosion layer whereas fast diffusion allows for the formation of a protective corrosion layer rather quickly.

3.1 Surface Corrosion

Samples exposed to the vapour phase (water saturated CO\(_2\)) show no dependence on exposure time or method of heat treatment. Corrosion rates remain nearly constant at approximately 0.004 mm/year. The carbonate layer is sufficient thick and can act as a diffusion barrier and reducing mutual diffusion of ions (CO\(_3^{2-}\) and O\(_2^{-}\)-species) into the steel and Fe-ions towards the outer surface (Pfennig et al., 2015).

In the liquid phase (CO\(_2\)-saturated saline aquifer) the corrosion rates increase, then decrease due to the formation of a passivating layer, and then increase again. This phenomenon (increase/decrease) is stronger for coupons immersed into the CO\(_2\)-saturated brine (corrosion rates around 0.004 to 0.014 mm/year). This may be due to the break-down of the passivating layer allowing the rather fast mutual diffusion of gaseous CO\(_3^{2-}\) and O\(_2\) -species into the metal and iron towards the surface where mainly siderite FeCO\(_3\) layers are formed (Figure 1) (Pfennig et al, 2013; Pfennig, Wiegand et al., 2013). Large areas of the corrosion layer may locally detach lateral to the surface enhancing and accelerating new processes at a fresh surface. Specimens exposed to CO\(_2\)-saturated saline aquifer form a carbonate layer because the siderite FeCO\(_3\)-solubility in CO\(_2\)-containing water with rather low pH is low after carbonic acid has formed (Cvijović and Randković, 2006). These heterogeneous corrosion scales of different magnitude cover the specimens` surface and pits. Main phases are: siderite FeCO\(_3\) and cementite Fe\(_3\)C. Also, goethite α-FeOOH at 100 bar and mackinawite FeS, akaganeite Fe\(_8\)O\(_8\)(OH)\(_8\)Cl\(_{1.34}\) and spinel-phases of various compositions are present at ambient pressure (Pfennig et al., 2015; Pfennig and Kranzmann, 2017).
Han et al., 2008 introduced a crack initiation model which was modified by Pfennig et al., 2016, 2013) applying for all states of heat treatment after exposure to CCS environment at 60 °C.

The three phase boundary during intermission of the CCS-process leads an unusual corrosion formation characterized by corroded ellipsoidal regions (Pfennig et al., 2017; Pfennig et al., 2016; Pfennig, Wolthusen, Wolf, Kranzmann, 2014). Siderite FeCO$_3$ and goethite $\alpha$-FeOOH passivate the remaining surfaces. The leopard structure is a consequence of the decreasing water solubility in supercritical carbon dioxide (Banaś et al., 2007). As shown in Figure 1 thin and small water droplets cover the metal surface that then consolidate (Pfennig et al., 2016). The initial ferrous hydroxide film is mechanically and/or chemically damaged and the highly porous non-protective ferrous carbonate is exposed directly to the geothermal water. Because these reactions result in a decreasing pH of the surrounding water the ferrous carbonate film dissolves and the steel depassivates. Then small pits that contain sulphates (FeSO$_4$) precipitating from the brine are formed and centered on the edges of former droplets (Figure 1). The former droplet center mainly reveals hematite (Fe$_2$O$_3$) (Han et al., 2008; Pfennig and Kranzmann, 2017). The flowing corrosive media removes the remaining film causing the pit to grow wider.

Independent of heat treatment, atmosphere (liquid, supercritical/vapour) or pressure (1 bar, 100 bar) the corrosion rate for X20Cr13 and X46Cr13 as well as X5CrNiCuNb16-4 is below 0.04 mm/year. High pressure in accordance with high CO$_2$ partial pressure reduced corrosion reactions and the lower corrosion rates after long exposure are likely to blocked capillaries within corrosion layers of adequate thickness that prevent fast diffusion. Therefore supercritical CO$_2$ possesses inhibiting function.
The influence of the corrosion behavior on the heat treatment of steels prior to exposure has been widely described (Alhajii and Reda, 1993; Pfennig et al., 2013; Bülbül and Sun, 2010; Zhang et al., 2008; Bron et al., 2004; Pfennig et al., 2014; Pfennig et al., 2017) (Figure 2). All corrosion rates of the steels investigated in this study increase with exposure time. Whereas in comparison to X5CrNiCuNb16-4 the corrosion rates of both heat treated martensitic steels X20Cr13 and X46Cr13 strongly increase by a factor of 3 at ambient pressure there is no increase at 100 bar (Figure 2) from 4000 h to 8000 h.

With exception of steel specimen hardened and tempered at 700 °C the corrosion rates of X20Cr13 and X46Cr13 are similar at 100 bar to those measured for the higher alloyed steel X5CrNiCuNb16-4 (below 0.005 mm/year). After long exposure times all specimen show similar corrosion rates with exception of steel specimen of X20Cr13/X46Cr13 hardened and tempered at 700/755 °C. Possibly chromium carbides precipitate and deplete the metal matrix so that no chromium oxide passivation layer may be formed and the steel degrades after long exposure times.

At 100 bar all graphs are parallel indicating that the heat treatment seems to influence the corrosion rate less than at ambient pressure. It may be assumed that heat treatment for X5CrNiCuNb16-4 plays a minor role with chromium content and atmosphere being more decisive. Hardened or hardened and tempered coupons give lowest corrosion rates at ambient pressure (Figure 2). Taking into account surface corrosion only, at 100 bar martensitic microstructure (hardened and tempered at 650 °C for the supercritical phase: < 0.001 mm/year) is preferred in water saturated supercritical CO₂. In CO₂ saturated aquifer water, however, normalized microstructure show good corrosion resistance (ca. 0.004 mm/year) (Pfennig et al., 2016).
Figure 2: The role of heat treatment on the corrosion rate of X5CrNiCuNb16-4 at 60 °C exposed to CO₂ saturated saline aquifer water at 1 bar and 100 bar (top (Pfennig et al., 2013; Pfennig and Kranzmann 2014) and in water saturated supercritical CO₂ (bottom) at 100 bar (Pfennig et al., 2013) in comparison to the corrosion rate of X20Cr13 and X46Cr13 (Pfennig et al., 2013; Pfennig et al., 2014).

In general corrosion rates for X5CrNiCuNb16-4 are low due to the passivating nature of the steel with even lower corrosion rates in the supercritical than in the liquid phase. Possible explanations are the lack of electrolytes (Pfennig et al., 2013; Pfennig et al., 2016) or the cathodic reactions described in equation (1) and (2). With a higher H₂CO₃ concentration the
environment becomes more acidic and reactive compared to the CO$_2$ saturated liquid phase (Seiersten, 2001; Banaś et al., 2007). For X5CrNiCuNb16-4 all corrosion rates increase at 100 bar in the supercritical phase indicating fast reaction kinetics and depassivation of the steel surface while the corrosion rates for specimen kept in the aquifer water remain at approximately 0.003 mm/y after 4000h and do not increase further with no regard to heat treatment. Due to carbide formation the initial passivating layer deteriorates after 1000 h of exposure (Figure 3, left). Because chromium is used to form carbides surface passivation – dependent on excess free chromium- is prohibited (Pfennig et al., 2016).

![Figure 3: left: SEM micrographs and composition of the ellipsoidal corrosion layer formed on 1.4542 hardened and tempered at 670 °C prior to exposure after 8000 hours of exposure at 60 °C and 100 bar to water saturated supercritical CO$_2$](image)

**3.2 Local Corrosion**

Pit intrusion depths generally increase with exposure time (Figure 4). Because pits reveal similar corrosion products as the surface corrosion layer it is necessary to separate these from saline precipitations such as CaCO$_3$ as seen in Figure 3, right. The presence of chlorides enhances local corrosion of the microstructure (Pfennig et al., 2016) as well as a high number of dislocations, grain boundaries, precipitation at phase boundaries, such as carbides. As a consequence local lattice mismatch leads to higher local boundary energy (Vignal et al., 2007) leaving the steel highly susceptible to corrosive attack of the CCS environment.
Figure 4: The role of heat treatment on the local corrosion of X5CrNiCuNb16-4 at 60 °C exposed to CO₂ saturated saline aquifer water at 1 bar and 100 bar (top partly taken from Pfennig et al., 2016 and in water saturated supercritical CO₂ (bottom) at 100 bar (Pfennig et al., 2013). Results are compared to the local corrosion of X20Cr13 at 60 °C, partly taken from Pfennig et al., 2013 and Pfennig et al., 2014.

Overall the penetration depth is independent of the heat treatment, showing lower intrusion depth (8-25 μm) for X20Cr13 and X46Cr13 after normalizing and hardening+tempering at 600 °C (Maximum intrusion depths ca. 300 μm for hardened X20Cr13 and a little lower for X46Cr13). For X5CrNiCuNb16-4 hardening+tempering from 670 °C to 755 °C offer low penetrations depths (10μm) (Pfennig et al., 2014) (10-250 μm average pit depths after exposure at 100 bar and 60 °C).

Figure 4 (Pfennig et al., 2013; Pfennig et al., 2016) normalizes comparable results obtained for X20Cr13 and X46Cr13 revealing smallest number of pits after 6000 h for hardening.
and tempering 600°C-670°C. Unusual low numbers of pits are likely because pits consolidate to shallow pits. At ambient pressure the number of pits are similar (<40,000 per m²) for X20Cr13, X46Cr13 and X5CrNiCuNb16-4. At 100 bar X5CrNiCuNb16-4 shows a high number of pits per m² in both atmospheres (Figure 6) (Pfennig et al, 2014). In general the number of pits formed in the supercritical and liquid phase is the same with exception for samples heat treated and hardened and tempered at 670 °C. There is no significant dependence of local corrosion phenomena on the heat treatment prior to exposure. Although X5CrNiCuNb16-4 is known as corrosion resistant in CCS environment it exhibits a significantly high number of pits at ambient pressure and 100 bar.

3.3 Corrosion Fatigue

The distinct corrosion fatigue behavior was described earlier by Pfennig et al. 2017, Pfennig et al., 2016 and Wolf et al., 2016). But, because these results were very unusual the fatigue tests were redone with a different charge of samples and newly artificially produced laboratory aquifer water (Figure 5). These results have been presented at ICBEE 2018.

Earlier results showed that the S-N-curve did not show expected fatigue strength and non-linear very steep slopes of possible fatigue strength for finite life (Wöhler-exponent of k = 3.59, scatter range TN=1:34, very small coefficient of correlation r² = 0.33), max. number of cycles (10 x 10⁷) at Sₘₐₓ=150 MPa) (Figure 6, bottom). Although the scatter range is much smaller, the slope of the fatigue limit line is still very steep indicating fast degradation of the material and resulting in an even lower max. number of cycles (10x10⁷) at Sₘₐₓ=130 MPa). The corrosion fatigue strength of X5CrNiCuNb16-4 is 60% lower than the endurance limit measured in air (620 MPa) (Pfennig et al., 2016), with steeper slope of the fatigue limit line as a function of increasing number of cycles (Pfennig and Kranzmann, 2017; Wolf et al., 2016).
Figure 5: S-N-curve and crack formation on 1.4542 exposed to saline aquifer water and technical CO$_2$. For comparison results from former experiments are given (Wolf et al., 2016)
No correlation was found regarding artificial aquifer water (Pfennig and Kranzmann, 2017) stress amplitude and number of failures, with increasing stress not inevitably leading to a lower number of cycles as expected. However, Aluminium was measured and heterogeneously distributed non-metallic inclusions were detected in the martensitic structure embedded with δ-ferrite (Figure 6, bottom) for samples with presumably short number of cycles to failure (Pfennig et al., 2016). This finding is appointed to this particular charge of the alloy, because in general it could not clearly be stated that Aluminum found within the microstructure leads to lower number of cycles and unpredictable early failure (Pfennig et al., 2017). X5CrNiCuNb16-4 reveals multiple cracks that are easily backtracked to pits as source of crack initiation. Inclusions, Aluminum and corrosion layer do not significantly influence the endurance limit – neither during the first fatigue testing nor the second. In general, early failure could not be related to

- Stress Amplitude,
- Impurities within the Microstructure
- Precipitation and Thickness of the Corrosion Layer
- Number of Striations.

As a consequence of the mechanical load the local boundary energy within the microstructure of the steel is increased due to local lattice mismatch (Pfennig et al, 2013) resulting in enhanced local corrosion as a result of:

- chlorides (Unigovski et al., 2009)
- Increased Dislocation Number
- Grain Boundaries
- Precipitation Phase Boundaries and Carbides.
The application of a cathodic potential proofed to enhance the corrosion fatigue life expectancy by a factor of 20 to 70. The potentials $U_{\text{SHE}} = -400$ to $-150$ mV only covered cathodic domains (Figure 7). Depending on the potential applied the deterioration was slower (low potentials) or faster (high potentials). A decreasing potential leads to the increase of the alloy’s corrosion fatigue life expectancy i.e. to an increase of number of cycles to failure. Runout specimens were loaded within the potentials $U_{\text{SHE}} = -150$ to $-400$ mV (preset threshold of $10^7$ cycles, no mechanical failure). Note, a cathodic potential discharges hydrogen from the specimen’s surface, enhances embrittlement of the alloy and may then lead to unpredicted and earlier failure.
Figure 7: CF life expectancy of X5CrNiCuNb16-4 with applied potential; isolated test set up, polished surface finish, push/pull load

4. Conclusion

The corrosion process and corrosion fatigue behavior of martensitic stainless steel 1.4542 was investigated to predict reliability of the steel in geothermal environment. At 100 bar as well as at ambient pressure and 60 °C hardening and tempering at low temperatures (600 to 670 °C) for 1.4022, 1.4043 and 1.4542 result in lowest corrosion rates and reveal good resistance against local corrosion.

Surface corrosion resistance is better in supercritical CO₂, whereas pit corrosion resistance is better in CO₂ saturated brine. Non-uniform corrosion scales with differences in thickness cover the specimens’ surface are mainly composed of: siderite FeCO₃ and carbides, mainly Fe₃C. Generally, ellipsoidal surface corrosion regions appear after exposure of >4000 h revealing hematite Fe₂O₃ and iron sulfate FeSO₄, FeCO₃ and FeOOH – the latter also after
corrosion fatigue tests. CCS environment cuts the endurance limit of 1.4542 measured in air in half. No significant correlation could be found between inclusions, discontinuous phase distribution, and Aluminum content within the base alloy and early rupture. Inclusions at the fracture surface and its cross section, pit and intercrystalline corrosion are source of crack formation lowering the number of cycles to failure.

Pitting corrosion phenomena, which most likely lead to a notch-based initiation region propagating fatigue crack growth, can be successfully depressed applying an appropriate cathodic potential. During geothermal application the fatigue life expectancy can therefore be enhanced to a great proportion by cathodic protection.

**Acknowledgements**

This work was supported by the FNK (Fachkonferenz für wissenschaftlichliche Nachwuchskräfte) of the Applied University of Berlin, HTW and by IMPACT (EU-Project EFRE 20072013 2/21). The authors would like to thank Andre Gröber, Rainer Wiegand, Roman Simkin and Roman Afanasieiev for their worthy contribution to this paper.

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