Influence of geothermal environment on the corrosion fatigue behaviour of standard duplex stainless steel X2CrNiMoN22-5-3

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Abstract. In the geothermal environment corrosion fatigue may severely lower the lifetime expectancy of high alloyed steels. Therefore, the corrosion fatigue (CF) of duplex stainless steel X2CrNiMoN22-5-3 was investigated in the Northern German Basin electrolyte at 369 K using a specifically designed corrosion chamber. Although the failure mechanism is independent of surface roughness (low scatter ranges technical surface: TN=1:1.35, polished surface: TN=1:1.95), the life expectancy in purely alternating axial cyclic load to failure was clearly related to surface finish and applied stress amplitude. Specimen with technical surfaces tested at high stress amplitudes (>275 MPa) lasted longer (cycles to failure: P₅₀ at Sₐ₃₀₀ MPa=5×10⁵) than specimen with polished surfaces (cycles to failure: P₅₀ at Sₐ₃₀₀ MPa=1.5×10⁴). When applying a protective potential a significant increase of CF life range from 4.7×10⁵ (free corrosion potential) to 10⁷ cycles (potential range from U_SHE=−450 to −900 mV) was observed. Microstructural analysis of the CF damage revealed horizontal grain attack within corrosion pit cavities, multiple fatigue cracks and preferable deterioration of austenitic phase. At low stress pitting is the initiating crack growth process whereas at high stress amplitudes the formation of micro cracks is reason for crack propagation and failure.

1. Introduction

Materials for future applications in the energy sector have to meet new requirements due to the general energy transition. In geothermal energy as well as in oil and gas production engineering materials are loaded mechanically and at the same time exposed to highly corrosive environments. During geothermal energy extraction mechanically loaded components such as delivery pumps as well as components for conveying and filtration are additionally stressed by corrosive environment. Frequency of cyclic loading, temperature and chloride concentration of the corrosive media show strong influence on the corrosion processes with simultaneously applied mechanical stress [1]. Moreover, corrosion fatigue mechanisms are enhanced, especially in the case of steels with low chromium content [2], by the presence of chlorides [3], hydrogen sulphide (H₂S) [4] as well as CO₂ [5]. The endurance limit will decrease with increasing temperature, increasing mechanical load and decreasing pH in the case of high alloyed steels [6–9]. But in contrary, increasing chromium content of steels as well as internal compressive stress in surface region increases the endurance limit. Standard duplex stainless steel DSS X2CrNiMoN22-5-3 (AISI 2205) promises good resistance to corrosion fatigue because of its known high resistance to stress corrosion cracking [10] and resistance to corrosive mediums [11,12]. The austenitic-ferritic duplex structure combines positive properties of both phases, is well known for its mechanical strength, thus this type of alloys is used in heat
Different authors show a direct dependence of the mechanical and corrosion behaviour of various steel qualities on the surface roughness resulting from machining processes [14-20]. In general, smooth surfaces, deeper plastic deformations and compressive surface stress enhances corrosion fatigue behaviour [21-23]. The corrosion resistance increases with decreasing valley of depth on the surface for carbon steel [24], austenitic stainless steel [14,15] after shot peening [16] and ferritic stainless steel when Ra exceeded 0.5 µm [17].

Corrosion fatigue resistance of X2CrNiMoN22-5-3 has already been investigated under different environments by various authors [28-31]. First results of steel samples tested under in-situ geothermal conditions were presented [32-35] and are now combined. Still, these results cannot be used for the distinct applications in geothermal energy production. To examine the influence of the corrosive media on the CF behavior of X2CrNiMoN22-5-3, the specimens were tested choosing conditions similar to those occurring in geothermal energy production.

2. Material and Methods

2.1. Standard duplex steel X2CrNiMoN22-5-3 and Northern German Brine

The corrosion fatigue tests have been performed using duplex stainless steel X2CrNiMoN22-5-3, manufactured by Deutsche Edelstahlwerke GmbH. The fabrication was accomplished by means of continuous casting with a skiving finish, resulting in a rounded rod with 65 mm diameter. The alloy subsequently underwent tempering at 1050 °C, followed by water quenching. The latter operation allowed the alloy's phase condition to be stabilized, i.e. ensured the ferrite/austenite balance and the absence of intermetallic phases that might otherwise appear in case of a slower cooling process [29].

The duplex stainless steel was analyzed by spark emission spectrometry SPEKTROLAB M (Spektro) and by an Electron Probe Microanalyzer JXA8900-RL. Table 1 summarizes the chemical composition of the experimental alloy. The mechanical properties are provided in Table 2.

| phases | C | Si | Mn | P | S | Cr | Mo | Ni | N |
|--------|---|----|----|---|---|----|----|----|---|
| α & γ** | 0,0 | 0,4 | 1,8 | 0,0 | 0,0 | 22, | 2,9 | 5,6 | 0,1 |
| α* | 23 | 8 | 3 | 24 | 08 | 53 | 2 | 4 | 46 |
| γ* | 2 | 5 | 9 | - | - | 24, | 3,6 | 3,8 | 0,0 |
| γ | 3 | 7 | 9 | 19 | - | - | 20, | 2,1 | 6,5 | 0,2 |

*spark emission spectrometry SPEKTROLAB M (Spektro)
**Electron Probe Microanalyzer JXA8900-RL.

Table 2. Mechanical properties of specimens tested

| Alloy          | yield strength in MPa | tensile strength in MPa |
|----------------|------------------------|-------------------------|
| X2CrNiMoN22-5-3| 672                    | 854                     |

To determine the corrosion fatigue strength of X2CrNiMoN22-5-3 round samples with shoulder heads were used. The design of the specimen is based on the guidelines of standard DIN EN ISO 11782-1 and the recommendation of the FKM Research Issue 217. The geometry of the hour-glass shape allows the formation of a stress concentration region in the center of the specimen. The continuously decreasing diameter of the sample results in 12.5 mm minimum area. To exclude the large influence of heterogeneous surface qualities, the surface of the samples does not undergo 25 cm². To simulate common technological surface, one set of specimens was manufactured by means of precision turning
without additional surface finish. The second set of specimens was polished in the critical region of the specimen exposed to the corrosion medium. Synthetically produced geothermal energy has been used as corrosion medium fluid. This is modeled after the North German basin [30]. The chemical composition of the Basin is shown in Table 3.

### Table 3. Chemical composition of the Northern German Basin

|        | NaCl | KCl  | CaCl$_2$ | MgCl$_2$ | NH$_4$Cl | ZnCl$_2$ | SrCl$_2$ | PbCl$_2$ | Na$_2$SO$_4$ | pH value |
|--------|------|------|----------|----------|----------|----------|----------|----------|--------------|----------|
| g/L    | 98.22| 5.93 | 207.24   | 4.18     | 0.59     | 0.33     | 4.72     | 0.30     | 0.07         | 5.4 - 6   |

2.2. Test Set-up

The corrosion fatigue tests were performed on a Schenck-Erlinger Puls PPV test machine. The frequency during the tests was about 33 Hz. A corrosion chamber is directly fixed on the test specimen (Figure 1). Through these mounting an interaction with the test machine is excluded. During the experiment, the specimen is surrounded by the geothermal brine (Northern German Basin).

![Schematic set-up](image)

**Figure 1.** Schematic set-up of for in-situ corrosion fatigue testing [33-35].

The corrosion medium is set for a temperature of 369 K at a flow rate of $V = 2.5 \times 10^{-6}$ m$^3$/s. This results in a theoretical flow rate of $\omega_0 = 1.7 \times 10^{-3}$ m/s at the critical section of the specimen. The flow rate is generated by a specially designed electromagnetically powered gear type pump. During the experiment the corrosion medium flows from the reservoir to the pump finally into the corrosion chamber and back into the reservoir (Figure 1). The corrosion medium is heated in the reservoir with permanent temperature control via thermal sensors as well in the reservoir as in the corrosion chamber. A sensor in the pump logs the flow rate of the geothermal brine. For the electrochemical experiments at constant potentials a titanium/titanium-mixed oxide electrode was installed to provide the distinct potential. The web was directly installed in the corrosion chamber and had no electrical contact with specimen or chamber. As reference and to measure the free corrosion potential an Ag/AgCl electrode was used.

3. Results and Discussion

3.1. S-N-Curve Corrosion Fatigue

For reason of comparison the fatigue limit of duplex stainless steel X2CrNiMoN22-5-3 in non-corrosive environment of is about 485 MPa ($P_f = 50\%$, push/pull) after a test duration of $10^7$ cycles [33-35] Generally, linear regression was applied as follows:
(1) The slope of the curve with a SN-coefficient \( s_k = 8.78 \) has a steep descent. This is typical for steels under corrosion fatigue. The scatter range \( T_N \) is the quotient between the probability cycle value of 10 and 90\%. It is with is only 1:1.35 extremely low. This shows that the mechanism which leads to fatigue in all the specimens is the same.

\[
N_{50} = N_A \cdot \left( \frac{S_a}{S_A} \right)^{-R} \quad \text{for} \quad S_a \geq S_A 
\]

with:
- \( N_{50} \) 50\% probability cycle value
- \( N_A \) reference cycle value
- \( S_a \) reference stress value
- \( S_A \) selected stress value

(2) The \( R^2 \)-value may vary from 0 to 1, with the higher number indicating higher coherence and thereby higher statistical certainty. The remarkably high \( R^2 \) value in this specific case can be explained either by the scarce dataset or the same fatigue mechanism. Also, the \( R^2 \)-coefficient of determination evaluates is with 0.99 very close to 1.

In corrosive environment and free corrosion potential the maximum number of cycles of \( (9.2 \times 10^6) \) was established at a stress amplitude of 240 MPa (Figure 2). The slope of the curve with an SN-coefficient of \( k = 4.7 \) was higher for an insulated set-up compared to an uninsulated setup. It depended on the electrochemical potential which shifted into a more cathodic range. The two SN-curves start at higher stress amplitudes (ca. 400 MPa) at approximately the same point. However, with decreasing stress amplitude the SN-curves diverge.

Figure 2. CF X2CrNiMoN22-5-3 S-N curves; uninsulated and insulated experimental setup.

To investigate the influence of an explicit electric insulation on the CF behavior of the material, the additional insulating components were installed on the fatigue testing machine otherwise electrically grounded. The insulating setup chosen allowed electric shielding of the subsystem specimen/corrosion chamber. According to the insulating conditions the free corrosion potential values were grouped.
The free corrosion potential (also known as resting potential) was monitored during the entire experiment employing the in-house Ag/AgCl wire electrode. The resting potentials exhibited considerable fluctuations, whereby the specimen loaded with 310 MPa demonstrated the most stable behavior. The fluctuations observed were registered at all experimental stages, whereby the initial values ranged from approximately $U_{SHE} = -110$ to $-200$ mV. An abrupt potential drop was observed at the end of every experiment. The consistent potential fall began approximately 10 minutes prior to the termination of the corresponding experiment, indicating clearly an upcoming failure of the specimen. Similar potential behavior was observed previously [24].

The free corrosion potential measured via electrically insulated setup is summarized in Figure 4. The decrease of fluctuations in combination with the overall more stable free corrosion potential behavior was observed. The initial values shifted towards more noble level, while the initial value range got reduced to approximately $U_{SHE} = -5$ to $-65$ mV. Analogous to the uninsulated series, the failure of each specimen was characterized by a distinct potential drop in the final stage of the experiment. Previously installed electric grounding did not provide sufficient electric shielding of the specimen. The employment of additional insulating elements, thereby, must insistently be recommended for conducting comparable corrosion fatigue experiments via larger pulsing fatigue testing machines.

3.2. Electrochemical potential

To determine the critical potential at stress amplitude of 275 MPa, a principle general stress amplitude, eight specimens were tested at different potentials. The critical potential determines the maximum until which corrosion effects are repressed. Applying a potential in the cathodic range resulted in an increase of the number of cycles compared to the number of cycles measured in a free corrosion potential. The cathodic potential impedes the initiation of local corrosion (pitting) which is most likely reason for crack initiation, it thus comes to a significant increase in fatigue life. At a free potential (ca. -3 mV) the specimen reached $4.7 \times 10^5$ cycles at the stress amplitude of 275 MPa. Applying a potential of $-150$ mV the number of cycles increased to $2.6 \times 10^6$. The number of cycles ($5.4 \times 10^6$) continuously increased up to a potential of $-300$ mV (Figure 3). At a potential of $-450$ to $-900$ mV the specimen didn’t crack and reached $10^7$ cycles. But, at this potential hydrogen was visibly evolved from the specimen’s surface [32]. In contrary, applying an anodic potential caused a more rapid failure of the specimen due to severe pitting on the specimen’s surface.

![Figure 3. Influence of the electrochemical potential on CF under pure axial push/pull load (left, including the influence of hydrogen) and rotation bending load (right).](image)

3.3. Influence of surface condition

The surface roughness ($Rz=2.6–4.6$) does not influence the corrosion fatigue behavior within one set of experiments, but different surface roughness after different surface treatments have large impact. As
discussed in detail [34,35] polished surface finishes (approximate $R_Z = 1.4-1.59 \, \mu m$) resulted in a significantly lower degradation rate of the material compared to turned surface finishes (approximate $R_Z = 3.2 \, \mu m$) (Figure 4). However, at low stress amplitudes ($9 \times 10^5$ cycles) turned specimens showed higher life expectancy. But with increasing exposure to mechanical stress and corrosive environment polished surface finish exhibited a higher CF life range. Due to the lower slope of the S-N curve the life expectancy increases with test duration and decreasing stress amplitude due to the likely less micro-notches in for smoother surfaces. Notches in general lead to an additional stress concentration within the notch base region, promoting the formation of an eventual CF initiation and thereby an earlier failure.

In general, technical surfaces give and sufficiently high numbers of cycles to failure regarding corrosion fatigue in the active or passive state at low stress amplitudes in geothermal environment. For duplex stainless steel 1.4462 the equilibrium at 98 °C in the saline water of the Northern German Basin was 275 MPa. At high stress amplitudes technical surfaces are preferred to achieve high numbers of cycles to failure. Technical surfaces tested at stress amplitudes above 275 MPa (P50% at Sa 300 MPa=$5 \times 10^5$) endured more cycles to failure than polished surfaces (P50% at Sa 300 MPa=$1.5 \times 10^5$). Rather low scatter ranges (technical surface: $T_N=1:1.35$, polished surface: $T_N=1.1.95$) indicate no change in failure mechanism. At low stress pitting is likely to be the initial crack growth process whereas at high stress amplitudes the formation of micro cracks is reason for crack propagation and failure.

![Figure 4. Influence of surface finish quality [34,35] and local corrosion initiation on CF; S-N curves, insulated test set-up](image)

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\begin{align*}
R &= 1, f = 30 \, Hz, K &= 1 \\
X2 CrNiMoN 22-5-3 &\quad \text{Northern German Basin} \\
T = 369 \text{ k}, D_{crit} &= 12.5 \text{ mm} \\
\text{Push/pull} &\quad \text{insulated} \\
\end{align*}
4. Conclusions

The corrosion fatigue behavior of the duplex stainless steel X2CrNiMoN22-5-3 was investigated under different conditions in the circulating corrosive aquifer brine: Northern German Basin heated to 369 K. Therefore hour-glass shaped specimens with different surface finish were tested in a corrosion chamber under free and applied potentials. Under corrosive environment duplex stainless steel X2CrNiMoN22-5-3 reached the maximum number of cycles $4.2 \times 10^6$ at the stress amplitude of 290 MPa with no isolation of the specimen against the test machine. The maximum of $9.2 \times 10^6$ cycles was reached at the stress amplitude of 240 MPa with insulation. The slope of the S-N curve in the case of the insulated setup (slope coefficient $k=4.7$) was higher than that of the setup without a distinct electrical insulation, indicating more rapid degradation of the alloy.

The effect of an electric insulation of the subsystem specimen/ corrosion chamber was investigated via employing the additional insulating components. The free corrosion potential measured for the electrically insulated facility exhibited overall more stable values. Regardless the electric insulation each experiment exhibited an abrupt potential fall prior to the final specimen failure. Corrosion fatigue tests at constant cyclic load of 275 MPa under different electrochemical potentials detected the critical potential below which corrosion effects can be repressed. At a potential of $U_{\text{SHE}} = -450$ to $-900$ mV the specimen didn’t fail and reached $10^7$ cycles with hydrogen visibly evolving from the specimen surface.

A polished surface finish resulted in higher CF life expectancy when compared to the precisely turned surface finish. The rougher surface finish led to the increased degradation of the material and consequentially to a positive shift concerning the longevity of the specimen with polished surface finish. The advantage of polished surface increased with experimental duration. The evaluation of the in-house manufactured Ag/AgCl wire electrode had confirmed both reliability and durability regarding specific CF experimental conditions. The electric potential of this wire electrode was measured versus the reference Ag/AgCl glass electrode. The calculation of the electrode’s potential referred to the conformal potential of the SHE and resulted in the value of $U_{\text{SHE}} = -57 \pm 1.1$ mV.

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