Failure of Standard Duplex Stainless Steel X2CrNiMoN22-5-3 under Corrosion Fatigue in Geothermal Environment

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Abstract. Corrosion fatigue is well known to lower the lifetime expectancy of high alloyed steels. Duplex stainless steel X2CrNiMoN22-5-3 is a promising candidate to withstand both, corrosion and mechanical stress. Therefore, the corrosion fatigue (CF) was investigated in the Northern German Basin electrolyte at 369 K using a specifically designed corrosion chamber. CF damage was clearly related to lateral grain attack within corrosion pit cavities located perpendicular to the load applied. Additionally, multiple fatigue cracks and preferable deterioration of austenitic phase and intact ferritic phase. A delta-like micro crack structure and a curved path characterizes crack termination with little to no base metal deterioration. Crack initiation may be due to early pit formation resulting in depassivation but also due to local depassivation then resulting in pit formation – both initiation mechanisms lead to crack propagation and early failure.

1. Introduction
Because materials for future geothermal energy extraction applications in the energy sector such as delivery pumps as well as components for conveying and filtration have to meet new requirements due to being loaded mechanically and at the same time exposed to highly corrosive environments. Frequency of cyclic loading, temperature and chloride concentration of the corrosive media influence corrosion processes when mechanical stress is simultaneously applied [1]. Degradation by corrosion fatigue mechanisms increases for steels with low chromium content [2] and in the presence of chlorides [3], hydrogen sulphide (H₂S) [4] as well as CO₂ [5]. For high alloyed steels increasing temperature and mechanical load as well as decreasing pH enhance corrosion fatigue phenomena [6–9] whereas chromium content and internal compressive surface stress increases the endurance limit. Standard duplex stainless steel DSS X2CrNiMoN22-5-3 (AISI 2205) used in heat exchangers, refinery towers, desalination plants and other operational units of chemical and petroleum industries [10] reveals high mechanical strength [10] resistance to stress corrosion cracking [11] and corrosive mediums [12,13].

Corrosion fatigue was tested in the geothermal brine of the Northern German Basin at 98 °C from S_c 175 to 325 MPa [14-18]. 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 10⁷ cycles [15-18]. Under corrosion fatigue at free corrosion potential X2CrNiMoN22-5-3 reached the maximum number of cycles of (9.2 x 10⁶) at a stress amplitude of 240 MPa (Figure 1, left) [15-18]. Main surface
and pit precipitation phases are mainly carbonates or hydroxides (FeCO$_3$, FeOOH) independent of the original surface roughness [7,16].

Due to the rather low scatter ranges (technical surface: TN=1.1.35, polished surface: TN=1.1.95, Figure 1 right [15-18]) it may be assumed that the failure mechanism remains the same regardless of surface condition. This paper reveals microstructural analysis to provide deeper understanding of crack initiation, propagation and final failure of X2CrNiMoN22-5-3 under conditions similar to those occurring in geothermal energy production.

![Figure 1. S-N-curves of X2CrNiMoN22-5-3. Left: using an insulated experimental setup [15-18], right: comparison of corrosion fatigue behaviour as a function of surface structures [15-18]](image)

### 2. Materials and Methods

The corrosion fatigue tests have been performed using duplex stainless steel X2CrNiMoN22-5-3 (Table 1), manufactured by Deutsche Edelstahlwerke GmbH (yield strength: 672 MPa, tensile strength: 854 MPa). The fabrication was accomplished by means of continuous casting with a skiving finish where the alloy subsequently underwent tempering at 1050 °C, followed by water quenching ensuring the ferrite/austenite balance and the absence of intermetallic phases [16].
Table 1. Chemical composition of the specimens tested

| phases  | C  | Si  | Mn  | P   | S   | Cr  | Mo  | Ni  | N  |
|---------|----|-----|-----|-----|-----|-----|-----|-----|----|
| α & γ** | 0.023 | 0.48 | 1.83 | 0.024 | 0.008 | 22.53 | 2.92 | 5.64 | 0.146 |
| α*     | 0.02 | 0.55 | 1.59 | -   | -   | 24.31 | 3.62 | 3.81 | 0.07 |
| γ*     | 0.03 | 0.47 | 1.99 | -   | -   | 20.69 | 2.17 | 6.54 | 0.28 |

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

Synthetically produced geothermal energy has been used as corrosion medium fluid (North German basin [19], Table 2).

Table 2. Chemical composition of the Northern German Basin (pH=6)

| NaCl | KCl | CaCl₂ | MgCl₂ | NH₄Cl | ZnCl₂ | SrCl₂ | PbCl | Na₂SO₄ |
|------|-----|-------|-------|-------|-------|-------|------|--------|
| g/L  |     | x 2H₂O | x 6H₂O |       |       |       |      |        |
| 98.22| 5.93| 207.24| 4.18  | 0.59  | 0.33  | 4.72  | 0.30 | 0.07   |

Round corrosion fatigue samples (according to DIN EN ISO 11782-1 and the recommendation of the FKM Research Issue 217) of X2CrNiMoN22-5-3 with shoulder heads were manufactured without additional surface finish as well as polished in the critical region of the specimen. Using a corrosion chamber directly fixed on the test specimen [6-8,14-18]. The corrosion fatigue tests were performed on a Schenck-Erlinger Puls PPV test machine at 33 Hz, 369 K at a flow rate of the medium V*= 2.5×10⁻⁶ m³/s ensuring a theoretical flow rate of ω₀ = 1.7 × 10⁻³ m/s at the critical section of the specimen. To characterize surface corrosion SEM/EDX was performed using: Leo Gemini 1530 VP, acceleration voltage 15 kV. Non-descaled parts of the samples were embedded in a cold resin (Epoxicure, Buehler), cut and polished first with SiC-paper from 180 µm to 1200 µm under water and then finished with diamond paste 6 µm, 3 µm and 1 µm. Etching was done using different solutions, such as Beraha II. The measurement of the layer thicknesses and phase thickness as well as microstructure analysis were performed via light and electron microscopy techniques using the semi-automatic analyzing program Analysis Docu ax-4 by Aquinto. Additional analysis of the alloy’s chemical composition was gathered via Electron Probe Microanalyzer JXA8900-RL separately for each phase.

3. Results and Discussion
Fractographical analysis of the corrosion fatigue cracking was investigated via etched microsections. Figure 2 shows a typical cross section through a highly developed macro crack with significant residual surface opening. This is referred to as an entire major crack region. Generally, the crack path is normal to the direction of applied cyclic push-pull load and therefore predominantly perpendicular to the lamellar duplex phases [17]. Likewise, the crack propagates through austenitic and ferritic phases without any preferred or weakest propagation region.

Figure 2. Microsection of macro crack with significant residual surface opening. Etchant: Beraha II.

After initiation cracks propagate strictly linearly with a residual crack width of approximately 30 µm measured within the dedicated crack initiation region attributed to the oldest cavity area. Figure 2,
3 and 4 proof that the austenitic phase (light grey) was susceptible to degradation, while the ferritic phase remained uncorroded leaving straight crack lines. This selective deterioration indicates local electric potential dominance of the ferritic phase [17]. Element distribution measurements revealed significant differences regarding the content of those chemical elements most important for the corrosion resistance, such as molybdenum, chromium and nitrogen. The resulting lower PREN value (Pitting Resistance Equivalent Number) as standard measurement to determine corrosion resistance of stainless steels is 37.39 for the ferritic and 32.37 for the austenitic phase [17]. The lower the PREN the less corrosion resistant is the steel quality. Therefore, the austenitic phase clearly reveals lower corrosion resistance. Another possible explanation is the difference in lattice structure. The face cubic centred structure fcc of the austenitic phase contains large octahedral interstitial lattice voids with a mean diameter of: ca. 0.41 R (R=average atomic radius). On the other hand, the body cubic centred ferrite bcc is characterized by rather small octahedral interstitial lattice voids of: ca. 0.20 µm. Diffusion processes are significantly higher in structures with larger voids leaving austenite high susceptible towards the intrusion of corrosive elements from the brine, such as chlorides. Pitting is therefore initiated at the austenitic phase or within the phase boundary of austenite and ferrite.

Approximately 3 mm below the sample surface the crack propagation path reveals multiple secondary micro cracks (Figure 2). However, these micro cracks remained small in width and soon discontinued after initiation, leaving only a single major propagation path.

Besides corroded crack flanks corrosion pits precipitated that are associated with minor crack, such as micro cracks without significant residual opening (Figure 3). Horizontal corrosion within grains as well as along grain boundaries proceeds beneath the subsurface zone forming new localized corrosion cavities as soon as this distinct area of preferred deterioration has contact to the electrolyte, e.g. the geothermal brine. In addition to corrosion phenomena along the crack flanks (Figure 3) the crack’s cavity mainly shows degradation of the austenitic phase which may be of importance considering the initiation of the pits. Due to dissolution of the corrosion pit’s region, however, it is not possible to verify this assumption. However, fracture surfaces mainly comprise of the ferritic phase due to early local disappearance of the austenitic phase (Figure 3, right).

Two possible corrosion fatigue mechanisms are possible, both derived from corrosion fatigue in the passive stat where initial corrosion phenomena act as catalyst of fatigue crack initiation and formatio. The mechanical stress enhances fatigue and crack propagation with corrosive deterioration of the crack flanks as a secondary phenomenon. The first mechanism is derived from the local corrosion effects and the second from degradation of the passivation layer (Figure 4):

1. Pit formation: The CF mechanism may be explained by the initial formation of the corrosion pit, followed by the crack initiation and depassivation of the micro crack area. As a consequence, cracks propagate in the case of sufficient stress being present in the corresponding region leading to early failure of the material.
2. Degradation of passive layer: The CF mechanism may be explained by local destruction of the passivation layer leaving newly formed surface exposed to the surrounding corrosive media. Persistent slip bands formed as result of mechanical axial push-pull load at the surface enhance the surface area where pits are easily formed. Both, exposed surface area and pits increase the degradation of the non-passivated area which then consequently leads to micro crack formation. Both initiation theories will inevitably lead to crack formation and degradation of the microstructure within the crack flank region (Figure 4 right).

![Figure 4. Schematic failure routes during corrosion fatigue. Left: pitting results in depassivation and crack formation. Middle: Depassivation leads to pitting and crack formation. Right: Crack formation and degradation of the microstructure within the crack flank region.](image)

4. Conclusion
To evaluate the failure mechanism, degradation of the steel and crack initiation and propagation the microstructure of different corrosion fatigue samples were investigated via etched micro cross sections. The initial crack region is characterized by a linear path perpendicular to the load applied. Then the crack feathers apart until the crack termination region may be described as a delta-like micro crack structure with an overall curved path. The cavity of immediate subsurface zone is most likely related to the earliest crack cavity exhibiting considerable degradation of the austenitic phase. At the same time the ferritic phase remains undamaged. Crack cavities allocated to later crack formation is generally located deeper underneath the subsurface. Crack initiation may be due to early pit formation resulting in depassivation but also due to local depassivation then resulting in pit formation – both initiation mechanisms lead to crack propagation and early failure. No deterioration of the material is noticed close to the specimen’s axis. The appearance of corrosion pits results in horizontal grain attack of the austenitic phase, assuming the lower corrosion resistance of the $\gamma$-phase according to PREN and distinct structural related diffusion processes.

5. References
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