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Investigation of Corrosion Fatigue of Duplex Steel X2CrNiMoN22-5 3 Exposed to a Geothermal Environment under Different Electrochemical Conditions and Load Types

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Abstract

Corrosion fatigue (CF) of duplex stainless steel (DSS) X2CrNiMoN22-5-3 was investigated in in-situ geothermal conditions of the Northern German Basin (NGB). The influence of the load type on CF behavior of the alloy was examined by applying push/pull and rotating bending cyclic load to failure. The hour-glass shaped specimens with both polished and precisely turned surface finish were tested in corrosion chambers allowing for the permanent circulation of Northern German Basin electrolyte heated to 369 K. Additionally, the influence of a protective cathodic potential on the CF life expectancy was investigated by employing a potentiostat. The rotating bending cyclic load led to a higher CF life expectancy, which decreased with increasing duration of the experiment due to a higher deterioration rate of the material. The application of a cathodic potential caused a significant increase of the CF lifespan from 4.7×10^5 (open-circuit potential (OCP)) to 10^7 cycles (preset threshold cycle number) for the potential range from $U_{SHE} = -450$ to -900 mV. Microstructural analysis of the CF damage revealed horizontal grain attack within corrosion pit cavities, multiple fatigue cracks and preferable deterioration of the austenitic phase.

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1. Introduction

Corrosion fatigue (CF) is a phenomenon, which may occur in technological applications with simultaneous mechanical and corrosive load. This specific type of compound load is often present in the field of geothermal energy extraction and may lead to significant reduction of the component's service life and hence to malfunction or even premature failure of an entire facility. The knowledge of the CF behaviour of the material employed is thereby crucial for developing a trustworthy component with long service life expectancy.

It is known, that CF can be enhanced in the presence of chlorides, hydrogen sulphide (H_2S) and CO_2 [1–5]. Furthermore, the endurance of the material may be negatively influenced by an increase of temperature, increase of mechanical applied load and decrease of the pH value in case of highly alloyed steels [6–9]. On the contrary, the life span of a material can be positively influenced by increasing the chromium content and by the presence of internal compressive stress. The lack of a general model for a CF simulation is due to the majority of CF endurance predictions being based on the empirical data [10].

The following work investigates CF of the duplex stainless steel X2 CrNiMoN 22-5-3 (UNS S31803) under the geothermal conditions of the Northern German Basin. The specific stainless steel is well known in industry for its excellent general corrosion resistance [11, 12] and good resistance to stress corrosion cracking [13]. These characteristics, combined with high strength, make this alloy the most widely produced DSS today [14] and the desirable candidate for geothermal applications in the future. Several previous studies investigated the CF of this specific alloy [14–17], however, none of those were addressed to the corrosion fatigue under geothermal conditions.

2. Material and experimental setup

2.1. Material

The tested DSS alloy X2 CrNiMoN 22-5-3 was manufactured by means of continuous castingfollowed by an appropriate tempering and water quenching. This fabrication procedure assures proper final microstructure and absence of strength lowering intermetallic phases. It had been empirically proved that duplex stainless steel grades exhibit their optimal performance once the content of austenitic and ferritic phases is balanced. The equilibrium of both phases, therefore, became standard for this specific type of alloys [18]. In order to confirm the material's chemical composition, samples underwent an additional analysis by means of spark emission spectrometry SPEKTROLAB and by Electron Probe Microanalyzer. Table 1 summarizes the chemical composition of the alloy.

phases	С	Si	Mn	Р	S	Cr	Мо	Ni	Ν
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

Table 1. Chemical composition of the specimens tested (in mass percent)

*spark emission spectrometry SPEKTROLAB M (Spektro)

**Electron Probe Microanalyzer JXA8900-RL

Table 2 shows the major mechanical properties of the alloy. The high strength values result from the material's fabrication process, its dual balanced microstructure and of the additional alloying elements, in particular nitrogen [19, 20]. Fig. 1 depicts the alloy's microstructure obtained via etching prior to fatigue testing.

Table 2. Mechanical properties of X2 CrNiMoN 22-5-3; tested in longitudinal phase direction

Alloy	yield strength (MPa)	tensile strength (MPa)
X2CrNiMoN22-5-3	672	854



Fig. 1 Microstructure of experimental alloy prior to testing; (a) transversal and (b) longitudinal sections respecting the casting direction [18]. Etching: Beraha II

The chemical composition of the synthetically produced aquifer solution of the Northern German Basic [21] is given in Table 3.

rable 5 Chemical composition of the Northern German Basin electrolyte										
	NaCl	KC1	CaCl2 x 2H2O	MgCl2 x 6H2O	NH4Cl	ZnCl2	SrCl2+ 6H2O	PbC12	Na2SO4	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. Experimental setup

In order to investigate the influence of the load type on the CF alloy's behaviour, the two major experimental series, namely push/pull and rotating bending series, were accomplished. Due to the distinct nature of the mechanical load applied, the experiments were performed employing two different corrosion chambers. The chambers were developed, manufactured and tested specifically for the following CF tests. The push/pull experimental series were carried out on the horizontal fatigue testing machine Schenk-Erlinger Puls PPV. The experimental setup is shown in Figure 2.



Fig. 2 Experimental setup for the geothermal in situ fatigue testing; schematic representation.

The rotating bending experimental series were completed on the in-house designed rotating bending fatigue testing machine. On account of comparability the boundary conditions as well as the measuring devices applied were identical in both experimental series. Taking into account the rotation of the specimen, a modified OCP measuring setup was applied. Additionally to the Ag/AgCl wire electrode a brush was installed to establish direct contact with the shouldered section of the specimen Figure 2 shows the major components of experimental setup for the fatigue tests.

The design of both corrosion chambers allowed for advantageous installation of sensors and additional components in immediate proximity to the critical cross-section of a specimen. The volumetric constant flow of the corrosion medium, which was provided by the internally developed gear type pump, accounted to $\dot{v} = 2.5 \times 10^{-6} \text{ m}^3/\text{s}$. The theoretical flow velocity of the electrolyte at specimen's critical cross-section was therefore $\omega_0 = 1.7 \times 10^{-3} \text{ m/s}$. The electrolyte underwent preheating within the main electrolyte reservoir and was held at a constant temperature of 369 K via control unit and additional heater, which was installed directly prior to the corrosion chamber entry. The resulting temperature fluctuation did not exceed ± 0.3 K. The mean frequency of cyclic load applied accounted to 30-33 Hz. The open-circuit potential of the specimen was recorded by the shock proof Ag/AgCl wire electrode.

2.3. Specimen

The shape and dimensions of hourglass specimens were selected in accordance to the standard DIN EN ISO 11782-1 and to the recommendations of the FKM Research Issue 217 [22]. The critical cross-section of both specimen types is 12.5 mm in diameter; the total contact surface area did not undergo 25 cm² in order to minimize the influence of irregularities [23]. The schematic drawing of specimens for push/pull and rotating bending fatigue experiments are exhibited in Figure 3.



Fig. 3 Specimens for (a) rotation bending and (b) push/pull CF tests

The effect of electric insulation on the open-circuit potential of the specimen was examined via push/pull experimental series. The additional insulating components, which were manufactured of glass-reinforced epoxy and PVC, allowed insulation of the subsystem specimen/ corrosion chamber from the rest of horizontal fatigue testing machine.

The effect of the cathodic potential was investigated via potentiostat in push/pull experiments. Cathodic potentials were applied via additional net-shaped counter electrode, which was mounted inside the corrosion chamber in the vicinity of the critical specimen's cross-section, however, without establishing direct contact with the latter and allowing for sufficient electrolyte circulation. The cathodic potentials were applied by potentiostat under constant purely alternating load amplitude of 275 MPa.

3. Results and Discussion

3.1. Open-circuit potential OCP

The additional electric insulation of the otherwise electrically grounded fatigue testing machine lead to a decrease of OCP fluctuations and to a general stabilisation of OCP values (Fig. 4). The initial OCP values shifted towards more noble magnitude in response to insulation. Moreover, the range of initial values decreased from U_{SHE} (-110 to -200) to (-5 to -65 mV) applying the insulated test setup.



Fig. 4 Effect of electric insulation of fatigue testing machine (a) OCP behaviour of uninsulated and (b) insulated setup

The remarkable drop of the OCP values was observed during the ending phase of each test independently from the electric insulation and other variable parameters applied. The potential fall began approximately 10 minutes prior to the final mechanical failure of a specimen and became thereby an earliest termination indicator. The potential drop can be explained by the formation of cracks, the passive layer is destroyed and the newly formed crack surface comes into contact with the corrosive medium [24]. An analogous behaviour of the OCP was observed in earlier studies [8, 25]. Considering the observed effect of electric insulation, the following experimental series, i.e. the comparison of the surface finish influence as well as the rotating bending experimental series were accomplished on the setups employing distinct electric insulation.

3.2. Load cases

The goal of the research work was to obtain experiment S-N-diagrams are a wide spaced way to describe fatigue life expectancy of a material under specific conditions. Moreover, this type of a diagram allows straightforward comparison of the fatigue life span concerning the influence of additional parameters applied.

The reference fatigue tests in air appointed an endurance limit of 485 MPa for X2 CrNiMoN 22-5-3 considering 10^7 cycles as threshold reference. Figure 5 summarises the experimental data combined with the corresponding 50% probability S-N curves for both load types. The slope factors of rotating bending and push/pull experimental series accounted to k=8.2 and k=19 respectively. The higher slope coefficient value in case of rotation bending load was significant in the cycle range 10^5 to 10^6 and decreased with the increasing number of cycles. The S-N 50% probability diagrams converged at approximately 3.5×10^6 cycles or 30 experimental hours, eliminating the advantage of the rotation bending load.



Fig. 5 Rotation bending vs. push/pull cyclic load in situ geothermal NGB conditions; 50% probability S-N curves

The fatigue experiments in air show a lower decline of the rotating bending for the entire experimental cycle span including the endurance limit section, i.e. convergence or overlapping of push/pull and rotation bending S-N curves diagrams is nonexistent. The advantage of rotating bending load over the push/pull purely alternating load in case of steel alloys loaded in air could be approximated by the factor 1.11-1.25, which correlates well with the results obtained in the initial experimental period [26]. A more negative slope factor of the rotation bending experimental series can be explained with the dominant influence of corrosion degradation caused by corrosion.

3.3. Influence of the Electrochemical Potential

The applied potentials ranged from $U_{SHE} = -900$ to +100 mV and covered partially anodic and cathodic domains. The result obtained are summarised in Figure 6. The specimens loaded in an anodic potential domain exhibited the reduction of the CF life expectancy. The velocity of deterioration correlated with the value of potential applied, i.e. the increasing potential led to the decrease of the alloy's CF life expectancy. The potentials of the cathodic range led to a significant increase of cycles to failure. The advantage of cathodic potential and the related increase of cycles corresponded to the decreasing value of potentials applied. The specimens loaded within the potentials $U_{SHE} = -450$ to -900 mV reached a preset threshold of 10^7 cycles without indicating mechanical failure and were declared as runouts. Furthermore, the cathodic potential range led to an explicit discharge of hydrogen from the specimen's surface. The results obtained show that the manifestation of pitting corrosion, which was assumed as a notch-based

initiation zone of fatigue crack propagation, can be successfully hindered via application of an appropriate cathodic potential.



Fig. 6 Influence of applied potential on CF life expectancy of X2 CrNiMoN 22-5-3; polished surface finish, push/pull load

3.4. Microstructure of Corrosion Damage (Corrosion Fatigue Cracking)

The evaluation of the CF damage was accomplished by means of both optical and scanning electron microscopy (SEM). The direct contrasting juxtaposition of the damage observed was advantageous in terms of understanding the influence of load type on the formation of CF cracks. The investigated fatigue cracks were divided into major and secondary cracks. The major cracks, which lead to failure, were characterised by a well pronounced residual opening and macro dimensions. The major fatigue cracks occurred predominantly in immediate proximity to the specimen's critical cross-section and were responsible for the final mechanical failure of a specimen. The secondary fatigue cracks, on the contrary, exhibited micro dimensions and did not possesses noticeable residual opening. The latter cracks could therefore only be observed via sufficient magnification. Figure 7 shows an etched microsection of a major fatigue crack. The crack's propagation path lay predominantly perpendicularly to the direction of load applied and crosses both phases of the alloy without indicating a preferable propagation phase. The termination region showed moderate branching within the partially curved propagation path.



Fig. 7 Microsection through a major fatigue crack; precisely turned surface, push/pull load

Figure. 9 demonstrates a microsection through corrosion pit, which was associated with a secondary crack. The distinct horizontal grain attack with an enhanced deterioration within the boundary surface was registered in the pit cavity. The latter may indicate potential proneness of the alloy to intergranular attack in NGB environment. The remaining ferritic lamellae in the pit's cavity (dark) indicate preferable deterioration of the austenitic phase (bright). The propagation of a fatigue microcrack, which initiated in the base of the pit's cavity possessed an arbitrary path and no residual opening, emphasising relatively young age of this specific crack. This type of micro corrosion pits were identified due to the presence of corrosion stains in their immediate proximity. - It is supposed that under given experimental conditions, corrosion pit initiation has primary character. Initiated corrosion pits first grow in dimension reaching a critical size, being then followed by formation of a fatigue crack due to a notch effect.



Fig.9 Microsection through secondary crack; precisely turned surface finish, push/pull load. Etching: Beraha II

4. Conclusions

The type of cyclic load applied significantly influenced CF life expectancy of the alloy. The advantage of rotation bending load, however, decreased with increasing experimental duration due to the higher deterioration rate of the alloy. The rotation bending and push/pull S-N curves converged at approximately $4x10^6$ cycles. The surface finish quality is another factor that may contribute to the CF life span. The advantage of additional polished surface finish was registered for the cycle number >10⁶ and increased corresponding to experimental duration. The potentials applied in a cathodic range led to significant improvement of alloys life expectancy compared to the results obtained via OCP. Considering constant cyclic push/pull load of 275 MPa, no mechanical failure was observed for the cathodic potential range U_{SHE} = -450 to -900 mV, when employing specimens with polished surface. The latter recognition indicates eventual capacity for this type of protection in industrial applications. The corrosion damage observed consisted primarily of fatigue cracks combined with highly localized pitting corrosion. Closer investigation of corrosion pits revealed partially intergranular corrosion and deterioration of the austenitic phase.

References

- [1] J.P. Thomas, R.P. Wei: Corrosion fatigue crack growth of steels in aqueous solutions I: Experimental results and modeling the effects of frequency and temperature. *Materials Science and Engineering: A*, Vol. 159 (1992), Nr. 2, S. 205–221
- [2] L.J. Mu, W.Z. Zhao: Investigation on carbon dioxide corrosion behaviour of HP13Cr110 stainless steel in simulated stratum water. Corrosion Science, Vol. 52 (2010), Nr. 1, S. 82–89
- [3] Y.B. Unigovski, G. Lothongkum, E.M. Gutman, D. Alush, R. Cohen: Low-cycle fatigue behavior of 316L-type stainless steel in

chloride solutions. Corrosion Science, Vol. 51 (2009), Nr. 12, S. 3014-3020

- [4] C.M. Holtam, D.P. Baxter, I.A. Ashcroft, R.C. Thomson: Effect of crack depth on fatigue crack growth rates for a C–Mn pipeline steel in a sour environment. *International Journal of Fatigue*, Vol. 32 (2010), Nr. 2, S. 288–296
- [5] I. Thorbjörnsson: Corrosion fatigue testing of eight different steels in an Icelandic geothermal environment. *Materials & Design*, Vol. 16 (1995), Nr. 2, S. 97–102
- [6] A. Pfennig, M. Wolf, R. Wiegand, A. Kranzmann, C.-P. Bork: Corrosion Fatigue Behavior and S-N-curve of X46Cr13 Exposed to CCS-environment Obtained from Laboratory in-situ-experiments. *Energy Proceedia*, Vol. 37 (2013), S. 5764–5772
- [7] A. Pfennig, R. Wiegand, M. Wolf, C.P. Bork: Corrosion and corrosion fatigue of AISI 420C (X46Cr13) at 60°C in CO2-saturated artificial geothermal brine. *Corrosion Science*, Vol. 68 (2013), S. 134–143
- [8] A. Pfennig, M. Wolf, K. Heynert, T. Böllinghaus: First in-situ Electrochemical Measurement During Fatigue Testing of Injection Pipe Steels to Determine the Reliability of a Saline Aquifer Water CCS-site in the Northern German Basin. *Energy Procedia*, Vol. 63 (2014), S. 5773–5786
- [9] R. Ebara: Corrosion fatigue phenomena learned from failure analysis. *Engineering Failure Analysis*, Vol. 13 (2006), Nr. 3 SPEC. ISS., S. 516–525
- [10] P. Marcus, T. Magnin: Corrosion Mechanisms in Theory and Practice. New York, CRC Press, 2012, S. 545 572
- [11] S. Schultze, J. Göllner, K. Eick, P. Veit, H. Heyse: Selektive Korrosion von Duplexstahl. Teil 1: Aussagekraft herkömmlicher und neuartiger Methoden zur Untersuchung des Korrosionsverhaltens von Duplexstahl X2CrNiMoN22-5-3 unter besonderer Berücksichtigung der Mikrostruktur. *Materials and Corrosion*, Vol. 52 (2001), Nr. 1, S. 26–36
- [12] N. Arnold, P. Gümpel, T.W. Heitz: Chloride induced corrosion on stainless steels at indoor swimming pools atmospheres Part 2: influence of hypochlorite. *Materials and Corrosion*, Vol. 49 (1999), S. 140–145
- [13] T. Prosek, A. Le Gac, D. Thierry, S. Le Manchet, C. Lojewski, A. Fanica, E. Johansson, C. Canderyd, F. Dupoiron, T. Snauwaert, F. Maas, B. Droesbeke: Low temperature stress corrosion cracking of austenitic and duplex stainless steels under chloride deposits. *Corrosion*, Vol. 70 (2014), Nr. 10, S. 1052–1063
- [14] A. Pfennig, M. Wolf, C.-P. Bork, S. Trenner, R. Wiegand: Comparison between X5CrNiCuNb16-4 and X46Cr13 under Corrosion Fatigue. In: Corrosion 2014, San Antonio, Texas, USA, NACE International, 2014, S. Paper No.3776
- J. Vollmar, E. Roeder: Einfluß der Kerbgeometrie auf das Schwingungsrißkorrosionsverhalten des Duplexstahles X 2 CrNiMoN 22-5-3. Werkstoffe und Korrosion, Vol. 45 (1994), S. 378–386
- [16] I.-H. Lo, W.-T. Tsai: Effect of selective dissolution on fatigue crack initiation in 2205 duplex stainless steel. Corrosion Science, Vol. 49 (2007), Nr. 4, S. 1847–1861
- [17] R. Mathis: Initiation and early growth mechanisms of corrosion fatigue cracks in stainless steels. Journal of Materials Science, Vol. 22 (1987), Nr. 3, S. 907–914
- [18] R. Afanasiev: Corrosion fatigue of duplex stainless steel 1.4462 (X2CrNiMoN22-5-3) exposed to geothermal environment at 100 °C simulating the Northern German Basin. Bachelorarbeit an der HTW-Berlin, 2015
- [19] I. Alvarez-Armas: Duplex Stainless Steels: Brief History and Some Recent Alloys. *Recent Patents on Mechanical Engineeringe*, Vol. 1 (2008), Nr. 1, S. 51–57
- [20] J. Foct, N. Akdut: Cleavage-like fracture of austenite in duplex stainless steel. Scripta Metallurgica et Materialia, Vol. 29 (1993), Nr. 2, S. 153–158
- [21] R. Bäßler, J. Sobetzki, H.S. Klapper: Corrosion Resistance of High-Alloyed Materials in Artificial Geothermal Fluids. Vol. NACE Inter Nr. Corrosion 2013, Orlando, USA, paper 2327,
- [22] H. Buschermöhle: Vereinheitlichung von Proben für Schwingungsversuche. FKM Forschungsheft 217, 1996
- [23] Beuth Verlag GmbH: Korrosion der Metalle Korrosionsuntersuchungen Teil 1: Grundsätze DIN 50905-1:2009-09. 2009
- [24] J. Vollmar, E. Roeder: Auswirkungen des elektrochemischen Probenpotentials auf das SwRK-Verhalten des Duplexstahls X2 CrNiMoN 22 5 3 in NaCl-Lösung. Werkstoffe und Korrosion, Vol. 45 (1994), S. 444–451
- [25] J. Vollmar: Schwingungsrisskorrosionsverhalten des ferritisch-austenitischen Stahles X2 CrNiMoN 22 5 3 in 3% iger NaCl-Lösung unter definierten Korrosions- und Wärmeübergangsbedingungen. Kaiserslautern, Univ., Diss., 1994
- [26] D. Radaj, M. Vormwald: Ermüdungsfestigkeit: Grundlagen für Leichtbau, Maschinen- und Stahlbau. Berlin Heidelberg New York, Springer-Verlag, 2007