Hydrogen Embrittlement Mechanism in Fatigue Behaviour of Austenitic and Martensitic Stainless Steels

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Abstract. In the present study, the influence of hydrogen on the fatigue behaviour of the high strength martensitic stainless steel X3CrNiMo13-4 and the metastable austenitic stainless steels X2CrNi19-11 with various nickel contents was examined in the low and high cycle fatigue regime. The focus of the investigations was the changes in the mechanisms of short crack propagation. The aim of the ongoing investigation is to determine quantitatively the predominant processes of hydrogen embrittlement and their influence on the short fatigue crack morphology and crack growth rate. In addition, simulations were carried out on the short fatigue crack growth, in order to develop a detailed insight into the hydrogen embrittlement mechanisms relevant for cyclic loading conditions.

1 Introduction

The demand for more efficient and cleaner technologies leads to the impulse to establish hydrogen as an energy carrier, for example in the automotive sector. This field of applications is already in the centre of research for a long time, where an important focus is put on a reliable and safe fatigue life prediction for weight-optimized and cyclically loaded components.

Mechanically loaded components in automotive such as pressure vessels, pipes, valves and compressors, are often exposed to hydrogen environments. The combination of mechanical stress and hydrogen environment can lead to more rapid material failure resulting from hydrogen embrittlement effects. Various theories are known from the literature that try to explain and describe these hydrogen effects and their basic mechanisms, such as HELP, HEDE, AIDE or HESIV (see for example the overview article by Lynch [1]). These mechanisms define idealized behaviour for special conditions and their relevance is strongly affected by stress and medium. They can occur separately or in combination, so that different mechanisms can take the dominant role during crack initiation and crack growth.

Most of the research on hydrogen embrittlement of stainless steels deals with the characterization of long fatigue crack growth behaviour [2, 3] or the effect of hydrogen on monotonic properties obtained in tensile tests [4, 5]. There is only little information available about the mechanisms of crack initiation and early crack growth.

Hence, the aim of this study is the identification of the changing microstructural mechanisms of fatigue crack initiation and crack propagation of microstructurally small fatigue cracks resulting from the presence of hydrogen in one martensitic and in two metastable austenitic stainless steels.

The findings are intended to serve as a basis for a physically based simulation model which describes quantitatively the growth of microstructurally small fatigue cracks [6]. Short crack growth is determined by characteristic microstructural processes such as the growth of cracks along grain boundaries or slip bands, which is decisively influenced by the diffusion of hydrogen in the microstructure as well as by the phase transformation of the fcc γ-austenite to bcc α′-martensite at the crack tip. The interaction of these effects must be integrated in the model in a realistic manner.

Metastable austenitic stainless steels

Metastable austenitic stainless steels show a deformation-induced martensite formation during fatigue. This phase transformation of γ-austenite (fcc) into α′-martensite (bcc) occurs spontaneously, without any diffusion and a lattice-distorting effect, in which the respective atoms remaining neighbours in the metal lattice. For the phase transformation, the martensite starting temperature Ms (equation (1)) must be underran.

A threshold value for the transformation, which is determined by the difference of the free energies of both phases ΔG, is reached. A temperature-induced
transformation can only proceed below $M_S$, above $M_S$ a mechanical deformation energy $\Delta G_{\text{mech}}$ must additionally be applied. Above a high temperature $T_0$, no phase transformation is possible. The martensite starting temperature $M_S$ can be estimated using the following empirical equation [7]:

$$M_S = 1350 - 1665 \times (%C + %N) - 28 \times %Si - 33 \times %Mn - 42 \times %Cr - 61 \times %Ni$$

(1)

In addition to the martensite starting temperature, the equations for the Schaeffler diagram can also be used to characterize the material with regard to its tendency to martensitic phase transformation. It represents the phases present at room temperature in CrNi steels, for which nickel and chromium equivalents are calculated and plotted in the diagram. According to equation (2) and (3), the effect of the main alloying elements on the phase transformation is taken into account [7].

$$\text{Ni-equivalent} = %Ni + 30 \times %C + 0.5 \times %Mn$$

(2)

$$\text{Cr-equivalent} = %Cr + %Mo + 1.5 \times %Si + 0.5 \times %Nb + 2 \times Ti$$

(3)

### 2. Experimental setup and materials

The experiments were carried out on one martensitic X3CrNiMo13-4 (X3) and two metastable austenitic stainless steels. The basic composition of the austenitic stainless steels correspond to the X2CrNi19-11 (304L) and were alloyed (Table 1) with two different nickel contents (9.07% (X2-9) and 12.36% (X2-12)). The grain sizes of the X2-9 and X2-12 was on average 205 $\mu$m.

The nickel equivalent is 10.35 for the X2-9 and 13.715 for the X2-12. The martensite starting temperature $M_S$ is calculated to -276.86°C for the X2-12 and -82.59°C for the X2-9. Both the calculated values of the starting temperature and the nickel equivalents show that the X2-9 has a stronger tendency for a martensitic transformation than the X2-12. The composition of the X3CrNiMo13-4 is also shown in Table 1.

| Table 1: Chemical composition of the two metastable austenitic (X2CrNi19-X) and one martensitic (X3CrNiMo13-4) stainless steels studied (weight %) |
|---|---|---|---|---|---|---|---|
| Alloy | C | Si | Mn | P | S | Cr | Ni |
| X3CrNiMo13-4 (X3) | 0.023 | 0.42 | 0.61 | 0.018 | 0.001 | 12.38 | 4.41 |
| X2CrNi19 (X2-12) | 0.016 | 0.48 | 1.73 | 0.012 | 0.008 | 17.79 | 12.36 |
| X2CrNi19 (X2-9) | 0.014 | 0.53 | 1.71 | 0.010 | 0.009 | 18.05 | 9.07 |

Fatigue tests ($R = -1$) were performed with X2-9 and X3 specimens at $f=1$ Hz using a servohydraulic testing machine and with X2-12 specimens in a miniature test machine (Figure 1, described in detail in [8]) in laboratory air at room temperature. These tests were performed with precharged and as reference with non-charged specimens. The fatigue tests were carried out at different testing machines and stress amplitudes because the crack initiation period should be monitored in the LCF / HCF regime despite their different fatigue strengths.

### 3. Results, discussion and modeling concept

#### 3.1 Results: austenitic stainless steels
The fatigue tests were carried out at different stress amplitudes because the crack initiation period should be maintained in the LCF/HCF transition range, despite deviating fatigue strengths. In order to compare the crack growth of X2-9 and X2-12 in all loading conditions, the results of the fatigue tests were summarized in the da/dN-ΔK diagrams in figure 3. Both stainless steels show similar da/dN values in the considered ΔK range; however, the curves allow different statements about the crack growth mechanisms. The oscillating curves correspond to the expectation of short crack growth curves according to literature [6], due to a strong interaction of the propagation of microstructural short cracks with the microstructural features. In the case of X2-9, it can be observed that the curves of the precharged specimens have higher da/dN values both at low and higher ΔK values; thus short crack growth is significantly accelerated by hydrogen.

The X2-12 samples show a significantly higher scatter compared to the X2-9 and thus no clear tendency of a hydrogen effect on the short crack propagation. However, it can be assumed that the crack grows even more slowly. This can be explained by the changing of the mechanism of the crack growth from single to alternating sliding, which occurs earlier under the influence of internal hydrogen. Furthermore, it is known from the literature [9] that austenitic stainless steels with increasing nickel content show a reduction of the hydrogen susceptibility.

Due to the in-situ experiments, the characteristic crack initiation sites of the precharged and the reference X2-12 specimens could be identified (Figure 4). An analysis of the slip band morphology and the crack initiation shows significant differences between the reference and precharged specimens. The average distance between the slip bands is about 4.7 µm and 1.92 µm in the precharged specimens and in the reference specimens, respectively. While the minimum height is identical, the highest slip bands in the precharged specimens are higher compared with those in the reference specimens (0.14 µm to 0.08 µm, respectively). Also, Aubert et al. have found this effect in stainless steel 316L specimens [10]. For AISI 310s stainless steel specimens, Robertson shows an increase of the slip band height because of hydrogen [11]. These observations show that the present hydrogen leads to a localization of plastic deformation and formation of the higher slip bands, likely resulting from the HELP mechanism. Hydrogen reduces the flow shear stress and localizes the dislocation motion, which is responsible for the displacement in the shear planes.

In the reference specimens, the cracks initiated mostly at grain boundaries, often in slip bands inside a grain. In contrast, for hydrogen-precharged specimens it was found that cracks mostly form at grain boundary triple points. This observation suggests a predominant hydrogen mechanism. Because grain boundaries [12] represent deep traps, a very large fraction of the hydrogen will be stored there after the precharging. This holds true in particular for major defects such as grain boundary triple points. Following the HEDE mechanism, in such places a local decohesion occurs, and therefore cracks can preferably initiate at these locations.

Furthermore, the curves of the X2-9 reference specimens show a stronger dependence on microstructural barriers, which manifests itself in the form of more variable crack growth rates. In contrast, the precharged X2-9 curves show a reduced barrier effect, which means that the crack growth rate increases more quickly and shows less oscillation. The reduced barrier effect can be explained clearly by the HELP mechanism, because it facilitates the movement of the dislocations locally.
3.2 Results: martensitic stainless steel

To characterize the influence of hydrogen on the fatigue behaviour of the X3, fatigue tests were carried out on the servohydraulic testing machine. For this, uncharged specimens were tested both in a laboratory air atmosphere and in vacuum ($3.4 \times 10^{-5}$ mbar) and were observed with a far-field microscope. Thus the influence of the atmosphere could be taken into account. The tested reference samples showed a basic hydrogen content of about 2 wppm after preparation. The hydrogen content of the precharged specimens was about 4-5 wppm. Figure 6 shows the influence of the atmosphere and the internal hydrogen on the crack growth rate of the X3. The cycle of the crack initiation could not be detected exactly during every fatigue test, but the crack lengths at the first observation show a clear image of the harmful influence of the internal hydrogen. Up to approx. 10,000 cycles, nearly all reference samples and the precharged specimens have already formed cracks at air. First cracks initiate in the vacuum specimens approx. 10-15,000 cycles later. The detected cracks in the precharged specimens are already significantly longer than those at laboratory air. The respective crack morphologies show a clear influence of the atmosphere. Cracks in vacuum are less branched in the specimens than in the reference and precharged specimens. The crack propagation in the precharged samples is more transgranular than in the reference samples (more intergranular) (see Figure 5).

3.3 Modeling strategy

The short fatigue crack growth model considers the plastic deformation in shear bands and the deformation-induced martensitic transformation at the crack tip and is based on several previous works [13, 14]. To consider the influence of hydrogen on the shear deformation along slip bands, the local hydrogen concentration in the microstructure is calculated after every crack growth step.

Short crack growth & shear band model

The short crack growth model (summarised in Figure 7) is based on the stage-I crack growth model by Navarro and de los Ríos [15] and extended to simulate short fatigue crack propagation in a real two-dimensional polycrystalline microstructure by [13, 14]. The model describes the deformation of the crack and the deformation along shear bands at the crack tip. The crack
can freely open and slide, but crack closure effects are also considered in the simulation. Plastic deformation as sliding along shear bands occurs if the friction stress $\tau_{F,0}$ exceeds the maximum resolved shear stress in a slip system at the crack tip. For the numerical solution, a boundary element method is used and the crack and the plastic zone (shear bands) are discretized with boundary elements. According to Navarro and de los Rios [15], the crack growth per loading cycle is calculated by the determined range of the cyclic crack tip slide displacement $\Delta CTSD$ by the boundary element method (eq. 4):

$$\frac{da}{dN} = c_{CTSD} \Delta CTSD$$

with the material dependent constant $c_{CTSD}$, representing the irreversible part of plastic deformation at the crack tip. As the sliding along the shear bands is decreased as the crack tip approaches a grain boundary, the crack growth decreases until a shear band in the next grain is generated. This slip transmission through a grain boundary occurs if a critical stress intensity or critical shear stress on a slip system in the neighboring grain, calculated at the sensor elements located at a distance $r$ from the grain boundary, is exceeded ($\tau > \tau_{F,0}$).

The grain boundary resistance for slip transmission can be determined according to [15] by assuming that at the

$$\tau_{F,0} = \sigma_{c,0}$$

The sliding along shear bands can be characterized by the friction stress $\tau_{F,0}$ and can be determined with the cyclic yield stress $\sigma_{F,ykl}$ with equation (6):

$$\tau_{F,0} = \sigma_{F,ykl} - \sigma_{c,0}$$

(6)

The crack growth model is capable of reproducing the decreasing crack growth rate near a grain boundary, as seen during stage I crack growth. When the crack tip approaches a grain boundary, the crack growth decreases until a shear band is formed in the neighboring grain. The crack tip slide displacement as well as the crack growth rate increases due to the increasing plastic zone size. With this modelling approach the well-known oscillating crack growth rate in a metastable austenitic stainless steel, the model considers the deformation-induced martensitic transformation at the crack tip [14, 17]. According to Bogers & Burgers [18] and Olson & Cohen [19], the martensitic transformation (from $\gamma$ to $\alpha'$) occurs by shearing on two separate shear bands compatible to the Bogers & Burgers model. This criterion is evaluated after each crack growth cycle and the newly formed martensitic area at the crack tip extends in the direction of the calculated crack growth. The amount of shear deformation along each shear band determines the size of the generated martensite domain. The martensitic transformation is associated with a transformation-induced volume expansion within the domain and contains a simple shear and a uniaxial dilation (invariant-plane strain) to describe the true shape deformation.

**Fig. 7:** Schematic representation of the short fatigue crack growth model

**Martensitic transformation model**

To simulate the crack growth in a metastable austenitic stainless steel, the model considers the deformation-induced martensitic transformation at the crack tip [14, 17]. The experimental observations showed that hydrogen influences the shear band morphology, thus the sliding along shear bands as well as the slip transmission through grain boundaries (see Figure 4). To model this effect, the friction stress along the slip bands ($\tau'$) as well as the activation of new shear bands ($\tau''$) are assumed to be dependent on the local hydrogen concentration $c_{H}(x)$ [cf. 22]:

$$\sigma(x) = \sigma(1 + \varsigma_{e} \ c_{H}(x))$$

$$\tau'(x) = \tau(1 + \varsigma_{f} \ c_{H}(x))$$

(8)

(9)

The parameters $\varsigma_{e}$ and $\varsigma_{f}$ have to be adjusted to appropriately predict the experimentally observed fatigue crack growth rates. Due to this approach, the local hydrogen concentration is determined and calculated based on the following diffusion model.
Diffusion model

In the simulation, it is assumed that the hydrogen dependent material parameters ($\tau_c$ and $\tau_F$) are constant during the loading cycle. After the loading cycle, the slip along shear bands is further evaluated to calculate the crack growth rate, see eq. (4). After this step, the local hydrogen concentration is calculated based on the diffusion model and the parameters controlling the slip band activation and sliding ($\tau_c$ and $\tau_F$) are updated. The time increment $\Delta t_c$ for the diffusion processes are determined by the previously calculated incremental loading cycles $\Delta N$ for the crack growth and the loading frequency $f$:

$$\Delta t_c = \Delta N / f$$  \hspace{1cm} (10)

The diffusion model is based on the influence of the hydrostatic stresses on the chemical potential in the microstructure [20]. By applying Fick’s first and second law the following differential equation is used to describe the transient redistribution of the hydrogen concentration in the microstructure:

$$\frac{\partial c_H}{\partial t} = D \cdot \nabla^2 c_H + \frac{V_H D R T}{\nabla c_H} \sigma_h \frac{\partial c_H}{\partial t}$$  \hspace{1cm} (11)

The transient hydrogen concentration $c_H$ depends on the transient evolution of hydrostatic stresses $\sigma_h$ as well as the diffusion coefficient of hydrogen in the material $D$, the partial, molar volume of hydrogen $V_H$, the gas constant $R$, the temperature $T$ and the time $t$. The transient hydrostatic stress $\sigma_h(t)$ is evaluated in the short crack growth model and is calculated using the Einstein summation convention ($i=1, 2, 3$) by:

$$\sigma_h(t) = -\sigma_{ii}(t)/3.$$  \hspace{1cm} (12)

As the model evaluates the stresses at discrete time steps $\Delta t$, it is assumed that the stresses are constant in this interval, which is schematically represented in figure 8.

Simulation results and discussion

To verify the presented model, the simulation results are compared with experimentally observed cracks and crack growth rates.

Simulation results of uncharged specimens in X2-12

As seen in figure a)-c) the experimentally observed crack path and crack growth is compared with the simulation result. The crack growth is only calculated by equation (4) as no crack growth along a grain boundary is modelled. The irreversibility constant $C_{CTSD}$ is determined with 0.2 $\mu$m/cycle by comparing the calculated with the experimentally observed crack growth in Figure 9 c). The parameter for the slip band nucleation is evaluated from equation (5) with the endurose limit $\sigma_D=250$ MPa and the mean grain diameter $D_m=205$ $\mu$m and the friction stress chosen with $\tau_F=80$ MPa according to [21].

It can be seen that the crack growth rate of the left crack tip increases with increasing crack length. But this effect is less pronounced in the predicted crack path compared to the experimental data. This can be explained by the insufficient prediction of the right crack path.

Simulation results of precharged specimens in X2-12

Following the simulation of the crack path in an uncharged specimen, the crack path and crack growth as well as the martensitic transformation in a precharged specimen are calculated (Figure 10). The calculated right crack path has a good correlation whereas the left crack tip stopped at the grain boundary. The simulated martensitic phase at the crack tip is also shown in figure 10 a. The transformation only occurs if two compatible shear bands at the crack tip are activated. As this condition is not met during each crack growth, the simulated martensitic phase is not continuously...
generated along the simulated crack path in contrast to figure 10 b. The simulation predicts that the crack path does not follow one slip system, but grows by alternate sliding along two activated shear bands at the crack tip which is facilitated in the presence of hydrogen compared to the crack growth behavior in uncharged specimens. This effect supports the assumption that hydrogen facilitates the activation of shear bands at the crack tip.

![Figure 10](image)

Fig. 10: SEM-image with the calculated crack path and the calculated martensite phase (green) a), phase-image of the precharged X2-12, $\Delta\sigma/2=365$ MPa, $f=5$ Hz, $c_H=40$ wppm b) [cf. 19]

Conclusions

The results of \textit{in-situ} fatigue tests were presented, which were performed on two metastable austenitic stainless steels and one martensitic stainless steel at a test frequency of 1 Hz under varying tensile-compressive load in the LCF / HCF regime. The focus of the investigation was on the characterization of the hydrogen mechanisms which influence the crack initiation and the short crack propagation.

The analysis of crack initiation and short crack growth behaviour of the metastable austenite samples showed a significant hydrogen effect, the X2-12 showing less susceptibility than the X2-9 due to its high nickel content.

An influence on the slip band morphology was also discovered. Hydrogen changes the crack initiation sites from slip bands (transgranular crack initiation) to grain boundary triple points (intergranular crack initiation). This change can be explained by the HEDE mechanism. Microstructural small cracks grow with a significantly higher crack growth rate in hydrogen-precharged specimen and show a significantly lower tendency to oscillating curves in the da/dN-$\Delta K$ diagram. The change in the crack propagation can be explained by a reduced barrier effect of microstructural barriers, caused by a facilitated displacement movement, according to the HELP mechanism.

The material X3 shows an even greater dependence of the fatigue properties on the test atmosphere and the hydrogen content. Cracks propagate faster in the precharged samples due to the hydrogen content. The crack morphology changes due to the hydrogen content and hydrogen effects (HELP) from more transgranular to a more intergranular crack propagation in the precharged specimen compared to the reference specimen. In Summary, the larger the martensitic phase, the higher the increasing of crack growth rate caused by hydrogen.

The simulation results show that the presented model is capable of predicting the experimentally observed crack path and the crack growth behavior. Based on the experimental observation of the changing slip band morphology under the influence of hydrogen, it is assumed that the activation and sliding of shear bands is facilitated depending on the local hydrogen concentration. In the simulation, the hydrogen concentration in the microstructure is calculated based on a diffusion model taking into account the influence of the hydrostatic stress on the hydrogen distribution. The influence of the hydrogen on the slip band formation affects the crack path as seen in the precharged X2-12 leading to facilitated activation of a second shear band. The crack growth in the martensitic stainless steel is simulated in the uncharged condition where the crack growth is dominated by cracking along the martensite lath boundaries. A good correlation with the simulated crack path is achieved. The crack path could only be predicted if the stress for the activation of new shear bands is increased compared to X2-12. Further, the increasing grain boundary density supports facilitated crack growth along grain boundaries. Further simulations on the crack growth for the metastable austenitic stainless steel as well as the for the martensitic stainless steel for precharged specimens and specimens in compressed hydrogen could give a more profound understanding on the influence of hydrogen on the crack propagation.

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