Operando time- and space-resolved high-energy X-ray diffraction measurement to understand hydrogen-microstructure interactions in duplex stainless steel

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ABSTRACT

Local strain development in the microstructure of a commercial 25Cr-7Ni super duplex stainless steel was mapped using high-energy x-ray diffraction during cathodic hydrogen charging under constant uniaxial load. The infusion of hydrogen resulted in tensile strains in austenite grains, one order of magnitude larger than those in the ferrite. Most strain evolution occurred at the near-surface, with compensating compressive forces developed in underlying regions, with up to two-times more compression occurring in the ferrite than the austenite. The strains along the loading axis were more pronounced than in the transverse direction, in which mostly compressive strains developed in the ferrite.

1. Introduction

Hydrogen in metals is well-known to degrade both mechanical and corrosion properties, a phenomenon known as hydrogen embrittlement [1–3]. High-strength steels and stainless steels are highly susceptible to hydrogen-induced degradation, with the mechanism remaining not fully understood [4,5]. The infusion of hydrogen is in most cases due to the evolution of hydrogen by cathodic reactions in aqueous media, either (i) corrosion driven, or (ii) due to an applied cathodic potential to the steel for protection against corrosion. In corrosion, anodic reactions, in which the metal dissolves, provide the current to the cathodic sites where atomic hydrogen can be formed. The atomic hydrogen can be absorbed ultra-fast (seconds) into the material and lead to strain localization, which often results in local plastic deformation and void formation and coalescence, with the latter often transiting to the formation of micro-cracks [5,6]. Highly-alloyed super duplex stainless steels are very corrosion resistant and typically replace lower grade alloys in demanding applications where corrosion is the primary concern while high strength and ductility are also required. However, in some applications, such as in offshore structures, duplex stainless steels are cathodically protected to prevent localized corrosion [7,8]. Failures of cathodically protected components made of duplex stainless steel with coarsely-grained microstructures (> 30 μm) have been reported to be due to hydrogen-induced delayed cracking [8,9]. Research efforts to understand material degradation caused by hydrogen infusion in duplex stainless steel are, therefore, not only necessary to assess and extend the service life of the components in harsh environments, but also for an increased fundamental understanding of the hydrogen-embrittlement process on the atomic scale.

The interaction of hydrogen with the microstructure at both atomic/local scale and mesoscopic/macroscopic lengths has remained poorly understood due to the difficulty in detecting the hydrogen, in real-time, and its effects on various length scales [1,4,5]. Most studies on hydrogen-microstructure interactions have been done, ex-situ, using post-mortem fracture surface analysis with the aim to understand the failure mechanism caused by the hydrogen. It is generally accepted that the diffusible hydrogen in the microstructure is responsible for embrittlement [4,5]. However, hydrogen so far cannot be directly observed,
especially during operando studies. Therefore, theoretical simulations in atomic length scales are finding increasing usage for studying hydrogen-microstructure interactions \([5,10-14]\). Useful information about hydrogen occupation and trap sites has remained little understood from density-functional theory (DFT) calculations \([5,13,14]\). Numerical studies based on finite element modeling (FEM) have been used to study dislocation activities as well as strain and stress evolution associated with hydrogen-laden microstructures both in mesoscopic and macroscopic scales \([5,15]\). The most valuable information which can be obtained from computational studies is perhaps the understanding of the energetics aspect of hydrogen embrittlement, which seems to be a lasting difficulty for experimental studies. However, simulations have the drawback that they often consider ‘frozen’ conditions or make assumptions in order to render computations executable on reasonable length and time scales. Computational studies typically focus on volumetric effects of the hydrogen where atomistic events are not considered, or calculations are made on microscopic or atomic scales to access atomistic information which represents small volumes only. There are studies that aim to combine a variety of computational techniques to provide a wide spectrum of lengths and energy information, but this requires far more experimental inputs, as hydrogen-microstructure interactions have remained little understood \([4,5,10]\).

Experimental studies, on the other hand, are often incomplete and can be subjected to uncertainties, errors, or artifacts. For example, most reported works are results from short-term experiments that were performed, ex-situ, without providing real-time information on the degradation process. It remained unclear how data obtained from short-term ex-situ experiments can be used to extrapolate long-term behavior in practical applications. Hydrogen absorption, diffusion and its interaction with the microstructure are ultra-rapid, therefore, experiments have to be designed reality-relevant which requires investigations preferably in real-time under realistic operando conditions. Showing the position of hydrogen, even if possible, provides no direct information about its (dynamic) interaction with the microstructure. Atom probe tomography or secondary-ion mass spectroscopy, which have been used to detect hydrogen, are destructive and do not reveal the dynamic nature of hydrogen embrittlement. The data obtained via these delicate techniques, furthermore, may not necessarily represent the entire microstructure as, for example, the effect of the austenite spacing (a mesoscopic parameter) of duplex stainless steel, which has been known to be a life-determining factor for hydrogen embrittlement, requires analysis of far larger volumes to be captured, which is beyond the possibility of current technology. Only trapped hydrogen can be detected by such measurements, with confidence at least, although it is the diffusible hydrogen which mostly matters in terms of hydrogen embrittlement. Before the hydrogen is trapped at trap sites either interstitially in the host lattice or by carbides, most hydrogen will diffuse to grain boundaries. Therefore, in-situ studies under operando conditions using non-destructive techniques are needed to provide local information at both microscopic and macroscopic scales in real-time. There are far more experimental data of hydrogen-microstructure interactions needed to improve our understanding of hydrogen embrittlement of duplex stainless steel.

In this work, synchrotron high-energy x-ray diffraction (HEXRD) was employed to measure the lattice strain evolution of the austenite \((\gamma)\) and the ferrite \((\delta)\) phases of grade 2507 super duplex stainless steel during hydrogen charging under static uniaxial mechanical load. The strains were measured with a depth resolution of 20 \(\mu\)m of a tensile specimen for up to 10 h of electrochemical hydrogen charging. The work reported in this paper improved understanding of the earliest stages of hydrogen-induced material degradation in duplex stainless steel.

2. Experimental

The material investigated – The material investigated was a solution-annealed \((1150^\circ\text{C} / 1\text{ h})\) UNS S32750 super duplex stainless steel, provided by Sandvik Materials Technology. The chemical composition is listed in Table 1. The material was obtained as a bar material with a diameter of 121 mm. Tensile specimens with a gauge length of 25 mm, a gauge width of 3 mm, and a thickness of 1.5 mm were manufactured using electric-discharge machining (see Fig. 1), followed by final milling to remove the oxide scale. The samples were cut with the tensile axis along the rolling direction and with the surface facing to the normal plane of the bar. One side of the samples was then ground using SiC sandpapers down to P4000-grit mesh size (European scale), and the other side was kept at P1200-grit finish. These surface finishes were done to achieve two different surface deformation to mimic residual stresses that arise due to machining. However, no quantitative evaluation of the residual strains and stresses were carried out. The final thickness of the specimen was 1420 \(\mu\)m. The latter side was facing downward in the setup shown in Fig. 1. The microstructure in the cross-sectional view is shown in the optical micrograph in Fig. 2a, b showing equiaxed austenite grains embedded in the ferrite matrix. The average grain size of the studied microstructure was \(\sim 20\ \mu\)m. The phase fraction of the microstructure was nearly 50:50, with an average austenite spacing of approximately 20 \(\mu\)m. The microstructure was characterized using optical microscopy and scanning electron microscopy, and no precipitate or secondary phase was observed. Numerous specimens with varying hydrogen charging conditions were tested, but the results of one are reported in this paper only.

**In-situ HEXRD, while hydrogen charging** – An experimental setup, as shown in Fig. 1, was designed to perform in-situ HEXRD measurements. The electrochemical cell consisted of two glass windows and an upper and a lower part made of polylactic acid (PLA), manufactured using a commercial 3D printer. The lower part had an opening of 4 mm diameter, in which a tube was connected to, enabling electrolyte pumping into the compartment. The upper part had a lid roof allowing the bubbles formed during cathodic charging to escape. A Pt-mesh counter electrode was mounted to the upper part of the cell. The sides of the compartments were grooved for sample positioning. A commercial ultra-fast drying silicone (1 h) was used to seal the entire cell, including the specimen and glasses. A custom-designed load frame made of super duplex stainless steel (provided by Bohler, Austria) was used to load the tensile specimen to a macroscopic strain of 1.05 %. The specimen was held at a constant load to mimic real application and to evaluate the precursor stages that lead to delayed fracture. \[16\] The specimen was galvanostatically charged with hydrogen in 1 M NaCl solution, with a cathodic current density of 38 mA/cm\(^2\). No recombination poison was used that would increase hydrogen uptake. The charging was done for 9 h and 3 min at room temperature while simultaneously collecting diffraction patterns through the entire specimen thickness. The HEXRD measurements were carried out at the Swedish Materials Science beamline P21.2 at the synchrotron PETRA III at DESY, Hamburg, Germany. The photon energy was 96 keV (0.1291 Å), and the distance between the sample and the Varex 4343CT flat panel detector was about 1.6 m. LaB\(_6\) was used for geometry calibration. The sample surface was aligned to be parallel to the x-ray beam, which was 20 \(\mu\)m (vertical) times 55 \(\mu\)m (horizontal) large. The sample surface was defined as the position where the intensity of the transmitted beam through the specimen had its half intensity when sampling across the sample surface. To measure depth-resolved diffraction patterns, the sample was moved vertically in steps of 20 \(\mu\)m (z-axis) using a position-sensitive goniometer that had a travel resolution better than 1 \(\mu\)m. At
each z-position (height), a 2D diffraction pattern was recorded with an exposure time of 1 s. During each exposure, the sample was moved by 1 mm along the horizontal axis perpendicular to the beam direction to improve grain statistics, resulting overall in a serpentine sample movement (see Fig. 2c). Hence, the measurement at the surface contains diffraction signals from approximately 10 μm beneath the surface, and all other measurement points contain signals from a volume of 20 μm (beam size) × 1 mm (transmission length) × 3 mm (transmission width). The measurement time for each layer was 3.8–4.0 sec, defining the time resolution per step due to the summation of exposure time and dead time for stage movement. The sample was scanned from 150 μm above the upper surface down to 150 μm below the lower surface to capture the entire specimen during hydrogen charging. The time elapsed between two measurements at the same coordinate of the specimen was 366 s, which defines the time resolution of each region of interest with a depth (spatial) resolution of 20 μm. Each scan step contained information from approximately 50–100 grains. The diffraction measurements were undertaken first without hydrogen charging (reference condition), then with hydrogen charging (for 9 h 3 min), followed by hydrogen desorption measurement for one hour after terminating hydrogen charging. The diffraction patterns were collected and stored as tiff files, which were first background-subtracted, then integrated azimuthally in a range of ± 5° (data conversion from 2D into 1D) around the loading and perpendicular direction using pyFAI [17]. The intensities were normalized using the primary beam intensity, which was collected simultaneously to compensate beam fluctuation. Data analysis (1D-diffraction data) was performed using the Peak Analyzer module Fit Peaks (Pro) of OriginPro 2019b V9.6.5.169 software using a mixture algorithm of Lorentzian and Gaussian peaks for fitting, which gave the best fitting quality (better than 10⁻⁹). The obtained peak centers were used to calculate the lattice constants of the ferrite and austenite and their changes as a function of hydrogen charging time. The lattice constants were determined from the average of five Bragg reflections, namely 111, 200, 220, 311, and 222 for the austenite and 110, 200, 211, 220, and 310 for the ferrite (see Fig. 1), and named as ‘mean’ lattice strain. The sample was first scanned...
without hydrogen charging, and then the potentiostat was switched on to charge the specimen continuously with hydrogen while XRD measurements run simultaneously. Hence, the change in peak position \((d \text{ at time } > 0)\) versus the uncharged position \((d \text{ at time } = 0)\) was calculated and denoted as macro-strain \((-\Delta d_{\text{macro}} = d_{\text{time} > 0} - d_{\text{time} = 0})\), lattice strain as follows) [23–26]. The procedure for data analysis is summarized in Fig. 3. Since scattering angles are small at high energies, several complete diffraction rings are captured on the stationary area detector. By fitting the radial peak positions for each ring and azimuthal segmentation (binning size was \(10^\circ\)), the length of the scattering vectors is determined to a relative accuracy of \(10^{-4}\) or better. For a known strain-free lattice parameter, the length of the scattering vector can be expressed as a projection of the strain tensor in the direction of the scattering vector. If at least six scattering vectors with sufficient orientation distribution (which requires sample rotation) are measured, the complete strain tensor can be evaluated. Without sample rotation, the scattering vectors at \(0^\circ\) or \(180^\circ\) and \(90^\circ\) or \(270^\circ\) are sufficiently close to the sample surface normal and loading direction, such that the respective strain components can be evaluated [18]. The azimuthal angles \(90^\circ\) and \(270^\circ\) corresponded to the loading direction, and \(0^\circ\) and \(180^\circ\) showed the direction perpendicular to the loading axis and the surface of the specimen.

3. Results

Figs. 4 and 5 summarize the strain measurement results obtained for all ferrite and austenite grains as a function of position in the microstructure and time of hydrogen charging. Fig. 4 shows the strain evolution perpendicular to the loading direction, i.e., orthogonal to the sample surface, whereas Fig. 5 shows the developed strain along the loading direction. The lattice strain is the mean strain calculated from the strains for the most common five crystallographic orientations with the strongest Bragg reflection intensities (see experimental section). The strain maps show the development of strain throughout the sample thickness with the positions \(0 \mu m\) and \(1420 \mu m\) (y-axis) being the geometrically upper and lower surfaces of the specimen, respectively. The lattice strain evolution shown in Fig. 4 indicated that hydrogen infusion resulted in the development of tensile strains in the surface region of both phases, with the austenite showing more enormous strains than the ferrite. The tensile strains in the austenite reached up to \(1.7 \times 10^{-3}\) after \(9\) h of charging, which is about double the strains compared to the ferrite. The infusion of hydrogen into the microstructure is instantaneous and occurs more readily into the ferrite than the austenite [5]. When hydrogen enters the microstructure, it will immediately diffuse to grain boundaries, in particular, phase boundaries, as these regions are energetically most favored, as commonly reported in the literature [4–6,12,19–21]. This will increase the mismatch strain acting between ferrite and austenite grains [3,22]. Phase boundaries are sinks for hydrogen and are potential sites for trapping [19]. Hydrogen enters the ferrite and austenite at the same time but diffuses with approximately five orders of magnitudes higher rates through the ferrite than the austenite [11,12,19]. On the other hand, the austenite can trap more hydrogen due to more significant occupation sites (octahedral voids); therefore, these sites contribute to a higher solubility of atomic hydrogen in the austenite [4,5,10–12,19]. We observed the evolution of large lattice strains in the austenite, larger than that in the ferrite, which indicates
a more considerable amount of trapped hydrogen in the interstitial sites of the austenite and also more considerable lattice-hydrogen interactions. In comparison, the ferritic lattice expanded despite the faster diffusion kinetics of hydrogen, indicating less hydrogen trapping and less lattice interaction. It should be noted that XRD measures lattice changes. In our setup, all changes were induced due to the interaction of hydrogen with the lattice. Positional information about the hydrogen in the lattice or grain boundaries were assessed in light of earlier reports in the literature [1, 4–6, 10, 11, 13, 15, 19–21, 23–29].

The evolution of tensile strains can be explained by the occupation of interstitial sites [5, 10] and mobilized dislocations, a phenomenon known as softening [26, 30]. The evolution of compressive strains can be a result of compensation of the tensile strains due to load sharing between the phases. Load sharing among the ferrite and austenite has earlier been reported in duplex stainless steel, which changes upon hydrogen charging [3, 22]. Acting compressive strains lead to a contraction of the lattice, which reduces hydrogen uptake and/or discharge of dissolved hydrogen. Contraction of the ferritic lattice, or in general

Fig. 4. The evolution of the lattice strain (mean) of the austenite (left) and ferrite (right) along the direction perpendicular to the loading axis as a function of cathodic hydrogen charging and hydrogen desorption (begin at 9 h 3 min). The strain map shows the evolution of strain in the entire specimen’s microstructure (1420 μm thickness) within the gauge length area of 1 mm length and 3 mm width. The exposure volume was 20 μm x 1000 μm x 3000 μm). A lattice expansion (tensile strains) of the surface down to 80 μm occurred in both phases due to hydrogen infusion whereas alternating compressive and tensile strains developed in the bulk interior. Note the onset of lattice relaxation occurred when hydrogen charging was terminated (denoted as “desorption”). 0 μm is the position for the upper surface of the specimen shown in Fig. 1 and 1420 μm indicates the lower surface of the specimen. The upper surface was ground to 4000-grit and the lower surface ground to 1200-grit.

Fig. 5. The evolution of the lattice strain (mean) in the austenite (left) and ferrite (right) along the loading direction as a function of cathodic hydrogen charging and hydrogen desorption (begin at 9 h 3 min). The strain map shows the evolution of strain in the entire specimen’s microstructure (1420 μm thickness) within the gauge length area of 1 mm length and 3 mm width. The exposure volume was 20 μm x 1000 μm x 3000 μm). Compressive strains developed in ferrite grains on the upper surface (0 μm) whereas tensile strains developed in austenite grains. Bulk ferritic grains, in contrast, showed larger tensile strains in the ferrite than in the austenite. 0 μm is the position for the upper surface of the specimen shown in Fig. 1 and 1420 μm indicates the lower surface of the specimen. The upper surface was ground to 4000-grit and the lower surface ground to 1200-grit.
for both phases, can also be caused by the generated compressive strains due to accumulated hydrogen at grain boundaries, as observed by Wan et al. in alpha-iron [23]. Furthermore, the collapse of vacancies or voids, which is typical in steels subjected to hydrogen uptake, can also produce compressive strains [5,28]. Voids have been reported to occur upon cathodic hydrogen charging of super duplex stainless steel, which transited to the evolution of micro-cracks at the interphase boundaries [6]. Voids certainly are formed by plastic deformation, which may have occurred in surface austenitic grains as the formed strains (other than the applied load) were close to 0.2%. It is well-established that microplastic events far below the macroscopic yield can occur before macroscopic plastic deformation. Hence, it is likely that the surface austenite and possibly also ferrite grains underwent microplastic deformation due to the high concentration of hydrogen. The hydrogen in the lattice eases dislocation motion and generation, resulting in hydrogen-enhanced localized plasticity (HELP) [1,5,28] that may have given rise to the evolution of vacancies and also voids [1,6,28]. The formation of voids could explain the reason for the immense strain evolution in the surface region as voids usually create large strain fields in their closest vicinity in the lattice, which can result in the formation of cracks [1,6,25,28]. No matter what the exact mechanism for the hydrogen-induced compressive strain evolution was, compressive strains, especially when evolved in the ferrite, are beneficial to retard crack evolution, as only tensile strains/stresses lead to the formation of cracks [25]. This implies that the duplex microstructure provides a beneficial synergism between ferrite and austenite as such that the microstructural constellation is disfavoring crack evolution, in particular when compressive strains are acting, making duplex stainless steels superior to counterpart single-phase stainless steels [3,6].

Furthermore, the larger strains evolved in the austenite suggest a substantial reduction in the lattice bond strength, which potentially could lead to a rupture in later stages. Density functional theory based molecular dynamics calculation has shown that the grain boundary cohesive strength was reduced by up to 74% due to hydrogen infusion in the microstructure [26]. Hence, the tensile strains observed in the surface region suggest the evolution of early precursor stages of hydrogen embrittlement and the tendency of cracks to preferentially develop along the loading direction (such cracks were observed and reported in earlier works [31–33]) due to the immense strain gradients along the depth direction which may result in delamination cracking in later stages. The surface of both phases showed the evolution of large tensile strains, showing larger magnitudes perpendicularly to the loading direction, indicating potential failure direction.

The ferrite has typically been reported as being the more vulnerable phase to hydrogen-induced cracking due to its higher susceptibility to hydrogen embrittlement [3–5,9,10,23,24,26]. Our results suggest that the hydrogen-altered surface region is the most susceptible site to hydrogen-induced degradation. This altered ‘layer’ may further give rise to the evolution of a crack in the form of delamination fracture, whose crack propagation may also occur along the loading direction, as reported by Yousefi and Itoh [24]. They documented observations of fractured super duplex stainless steel that was subjected to cathodic hydrogen charging for 24 h using a current density of 10 mA/cm² and a recombination poison added to the electrolyte (this increases massively the uptake of hydrogen). Their results showed surface delaminated cracking, expanding over the entire hydrogen-charged specimen (see Figure 6 in their publication [24]). The delaminated layer had a thickness of ~60 μm, which is close to the thickness of the surface-altered region observed in our work (Fig. 4). Their fracture surface analysis showed that the delamination crack formed and propagated parallel to the loading direction along the flat-tensile specimen surface [24]. Hence, in light of the work of Yousefi and Itoh [24], our work suggests that the hydrogen-enhanced decohesion (HEDE) and HELP mechanisms well-likely have cooperated during hydrogen charging, which led to the evolution of severe tensile strains gradients, seen in Fig. 4.

Surprisingly, the surface grains of both phases showed the development of sizeable tensile deformation, both reaching depths down to 80 μm after 9 h of hydrogen charging. This indicates an interaction of hydrogen with the two phases in the microstructure, despite that hydrogen diffuses faster in the ferritic lattice than in austenitic one. The results suggest that the interaction of hydrogen with the two phases was of a similar time scale, and the austenite likely forms the rate-determining step, as it is supposed to provide a slower diffusion pathway for atomic hydrogen. The diffusion of hydrogen in duplex stainless steel is not a simple average of hydrogen diffusion in the ferrite and austenite. However, its kinetics is determined in the first instance by the phase fraction, constellation of the ferritic to austenitic grains (shape, morphology, orientation), and grain size [1,5,10,21]. In microstructures with small austenite spacing (ferrite grain size less than ~30 μm), the grain size is more influential because the invading hydrogen is more trapped at phase boundaries, and the austenite grains become faster saturated by hydrogen [6,21,30]. So, when hydrogen enters the microstructure, it diffuses with a higher rate in the ferrite. When it encounters an austenite grain, it circumvents that grain and proceeds, which is known as the ‘tortuosity’ [21]. However, it should be emphasized that some of the hydrogen atoms also enter immediately austenite grains, and due to the small size of the grains, hydrogen can permeate (and saturate) austenite grains (near-surface regions at least) in similar rates as the hydrogen circumvents the ferrite and passes by trap sites, or, the hydrogen atoms those enter the austenite cause considerable strain evolution (as detected in this work) before reaching the saturation point for hydrogen [21]. It is more likely that saturation or near-saturation of hydrogen in the austenitic grains at the surface occurred as the concentration of infusing hydrogen in the surface region is very high, providing abundant energy to surpass any barrier [20,21]. However, saturation below the near-surface region (>80 μm) cannot have occurred as this requires far longer charging times.

The surface of the specimen facing against the counter electrode (vertically upward, 4000-grit surface finish) showed tensile lattice strains down to 40 μm below the surface, whereas the other side (1200-grit finish) showed tensile strains up to 80 μm. Grinding, usually, introduces tensile strains to the surface region [24], so the coarser finish accelerated the hydrogen entry into the austenite lattice. Assuming the lattice expansion (tensile strain) caused by the absorbed hydrogen can be considered as the direct evidence for hydrogen diffusion; so the diffusion coefficient can be obtained by solving Fick’s second law [35]:

\[ x = 2\sqrt{Dt} \]

where \( x \) is the penetration depth of atomic hydrogen, \( D \) the diffusion coefficient, and \( t \) the time. This holds for situations where the initial concentration of the diffusible species is zero and where the surface concentration is maintained constant. Hence, in this simplified calculation, we obtain \( Dx = 10^{-15} \text{ m}^2/\text{s} \), which is very close to \( 10^{-16} \text{ m}^2/\text{s} \) as reported for austenite by Mente and Boellinghaus [11,12] and Hutchings and Turnbull [19]. In the duplex microstructure, this calculation also applies to the diffusion kinetics for surface ferrite grains, as explained above. So, this finding potentially explains the reason why duplex stainless steels show higher resistance to hydrogen embrittlement than stainless steels with ferritic microstructure. The penetration depth of hydrogen into the microstructure has been estimated using Fick’s second law and the diffusion coefficients that Mente and Boellinghaus [11,12] and Hutchings and Turnbull [19] have reported for the austenite and ferrite. Hydrogen could penetrate the austenite to a distance of 6.5 μm according to Mente and Boellinghaus [11,12] or 4.3 μm according to Hutchings and Turnbull [19]. So, it is very likely that austenite grains smaller than 8–12 μm were saturated with hydrogen (infusion occurs from all faces of a grain), in the first instance the grains at the surface, as the effective diffusion of hydrogen in duplex stainless steel is mainly determined by the ferrite, which has far higher
diffusivities than the austenite [19]. The hydrogen into the ferrite can reach to depths down to 882 μm according to Hutchings and Turnbull [19] and 1394 μm according to Mente and Boellinghaus [11,12]. As the hydrogen entered the specimen from both sides, all ferrite grains after 9 h were very likely saturated with hydrogen (half thickness of the specimen thickness was 710 μm). So, it is the surface that is always the most susceptible site to hydrogen-induced degradation, with the ferrite being first affected than the austenite. The degradation process is, furthermore, a delayed event that evolves as long as hydrogen infuses and interacts with the microstructure in the presence of residual or acting external stresses. Some failure of swaged super duplex stainless steel with very coarse microstructure has been reported that was caused by delayed fracture, which the ferrite was mainly made responsible for [8,9]. The increasing magnitude of tensile strains in the ferrite as shown in Figs. 4 and 5 suggest these as the most incipient stages of damage evolution. Along the loading direction, bulk ferrite grains showed the evolution of tensile strains, indicating elongation of grains. The latter indicates that hydrogen-induced softening of ferritic grains along the loading direction was operating [36]. It should, moreover, be noted that room-temperature creep at the given load is practically zero, so all strains that occurred were due to hydrogen-microstructure interactions.

Hydrogen embrittlement is a complex multi-faceted type of degradation that depends on various environmental and material factors. In duplex stainless steels, hydrogen-induced cracks have been shown to typically initiate first in the ferrite and extend to the austenite [6,30,37]. Hydrogen-enhanced localized plasticity and decohesion mechanisms can cooperate, but this is not possible to conclude if the proposed hydrogen degradation mechanisms act simultaneously or in a sequence. It is known that there is not a single mechanism responsible [26], and the ferrite shows a different mechanism than the austenite [24,36]. Our operando HEXRD results suggest that hydrogen-enhanced plasticity processes accelerated the evolution of microstructure, which established high local concentrations of strain associated with hydrogen accumulation. The results show that the interaction of hydrogen with microstructural features have different responses in both phases and across the specimen thickness. Hydrogen can move with mobile dislocations or activate them to glide [26]. The data corroborate the assertive statements of Beachem [29] that hydrogen-strain-microstructure interactions promote dislocation motion and generation. Our methodology revealed locations in which hydrogen caused most changes, suggesting these sites to be most vulnerable and, hence, providing a unique protocol for real-time investigations. It should be noted that XRD measures the lattice d-spacing, and the lattice strains observed were due to hydrogen-microstructure interactions. While infusing hydrogen into the lattice (both soluble and trapped) causes the formation of strains directly, hydrogen at grain and phase boundaries also contribute to the evolution of strains and stresses in the microstructure in an indirect way. This approach provides only indirect evidence of hydrogen in the microstructure. However, positional as well as temporal information of the effect of hydrogen in the entire specimen was successfully demonstrated which has provided unprecedented knowledge of hydrogen-microstructure interactions in a commercial super duplex stainless steel microstructure.

5. Conclusions

- Electrochemical hydrogen charging resulted in the formation of lattice tensile strain occurring more readily in austenite than ferrite grains.
- The strain evolution was more pronounced along the loading axis than perpendicular to it.
- Most strain formation occurred at the near-surface, which extended toward the depth with increasing charging time.
- Hydrogen-induced lattice strain development was highly heterogeneous, forming alternating tensile-compressive regions throughout the bulk material.
- Near-surface ferritic grains developed compressive strains perpendicular to the loading axis disfavoring, thereby crack formation.
- The austenite is the phase that undergoes most deformation and supports thereby the ferrite against hydrogen embrittlement.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Code availability statement

The codes and mathematic algorithms used for the production of the data will be made available by the corresponding author upon reasonable request.

CRediT authorship contribution statement

Cem Örnek: Conceptualization, Methodology, Software, Formal analysis, Investigation, Visualization, Data curation, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. Timo Müller: Methodology, Software, Formal analysis, Investigation, Data curation, Writing - review & editing, Visualization. Ulf Kivisäkk: Conceptualization, Methodology, Investigation, Resources, Writing - review & editing. Fan Zhang: Investigation, Software, Writing - review & editing. Marie Långberg: Investigation, Writing - review & editing. Ulrich Lienert: Methodology, Software, Investigation, Resources, Writing - review & editing. Ki-Hwan Hwang: Methodology, Writing - review & editing. Edvin Lundgren: Methodology, Writing - review & editing, Supervision, Funding acquisition. Jinshan Pan: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Data curation, Writing - review & editing, Project administration, Funding acquisition, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the
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