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Influence of prior austenite grain structure on hydrogen-induced fracture in as-quenched martensitic steels

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ABSTRACT

Suppressing hydrogen embrittlement in martensitic steels is a longstanding challenge. Here, we studied the effects of prior austenite grain (PAG) shape and size with a 0.25C steel utilising novel in situ H-charging, constant-displacement Tuning-fork testing (TFT) and H-permeation tests. Anisotropic elongated PAG structure has enhanced HE resistance transverse to the rolling direction (RD) with slower crack propagation rate (CPR) and quasi-cleavage fracture. Larger elongated grains are prone to intergranular fracture when crack propagates in RD. Reaustenitised equiaxed PAGs fail with intergranular cracking, which accelerates max CPR up to threefold compared to quasi-cleavage. All the microstructures have similar H-diffusion $\sim 5 \times 10^{-7} \text{cm}^2/\text{s}$ and density of reversible H-traps $N_T \sim 3 \times 10^{16}$, irrespective of PAG surface area, indicating that PAG boundaries are not effective diffusion paths. Deformed PAG boundaries mitigate susceptibility to intergranular cracking.

1. Introduction

High-strength steels are widely used in structural applications in automotive, mining, and agricultural industries. Increased strength facilitates the use of lighter structures, which are more efficient from the economic and environmental perspectives [1]. However, high-strength steels are also sensitive to hydrogen-induced fracture, i.e. hydrogen embrittlement (HE) or delayed fracture, which is becoming a major concern for the steel industry and complicates the broader utilization of these steels [2,3]. The susceptibility to hydrogen embrittlement is affected by numerous factors such as alloy composition, microstructure, mechanical properties, production route, environment, and applied stress level and state [3].

Generally, the strongest steels have a martensitic microstructure, which is formed by a near-diffusionless transformation in rapid quenching of austenite [3]. The complete suppression of carbon diffusion in quenching is virtually impossible due to auto-tempering. With high enough martensite start ($M_s$) temperature, carbon mobility is sufficient to cause cementite precipitation resulting in microstructure resembling tempered martensite [4,5]. A traditional route for producing high-strength steels is by reheating and quenching (RQ) of austenite subsequently followed by a tempering treatment (QT) to improve ductility and toughness [6]. With the conventional RQ process, austenite is always recrystallized before quenching, producing essentially equiaxed prior austenite grain.

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(PAG) structure in the final martensitic microstructure. Alternatively, martensitic high-strength steels can be produced by direct quenching (DQ), which is a thermomechanical rolling process integrated with immediately following quenching without additional tempering step \([1]\). DQ steels get auto-tempered, i.e. tempered during the remaining quenching below \(M_s\), which improves toughness without the additional reheating procedure required for QT steels \([1,5]\). Hot rolling of DQ steels can be conducted with either recrystallized or non-recrystallized austenite. In the case of rolling below the non-recrystallization temperature, the final martensitic microstructure will show microstructural alignment and have elongated/pancaked PAGs parallel to the rolling direction \([1,7]\). In addition to DQ, ausforming \([8]\) and tempforming \([9]\) treatments can also produce elongated PAG structures by utilizing even lower temperatures.

Hydrogen (H) can enter the steel only in its nascent/monoatomic form during the manufacturing processes and/or in-service environments \([3,10]\). After entering the steel, concentration gradient driven hydrogen diffusion, and trapping take place inside the material. Generally, H-assisted failure happens when diffusible H migrates and accumulates into regions under triaxial tensile stresses, and above a certain critical concentration, hydrogen embrittlement occurs. These stresses can be external and internal, the latter resulting in cold cracking \([11,12]\). H atoms diffuse interstitially or along grain boundaries and moving dislocations \([13,14]\). However, the rate of diffusion is slowed down when H is attracted and confined, i.e. trapped, by various microstructural features \([3,15]\). Depending on the microstructure, different types of hydrogen traps exist, such as vacancies, dislocations, grain boundaries, solute atoms, precipitates, inclusions, interfaces, and voids, that affect hydrogen solubility and diffusivity. Hydrogen traps can be divided into two categories according to their binding energy, irreversible (strong) and reversible (weak) traps. In high-energy irreversible traps, such as carbide interfaces or incoherent precipitates, hydrogen becomes immobile. Consequently, a homogeneous distribution of irreversible trap sites in the microstructure may improve HE resistance. Reversible traps, such as vacancies, dislocations, and grain boundaries, have a low binding energy and they can hold as well as release hydrogen. Therefore, diffusible and reversible trapped hydrogen can induce HE \([3]\).

The typical microstructure of high-strength steels is lath-martensite \((\text{C} \leq 0.6 \%)\), where each PAG transforms to numerous discrete bcc laths, which form crystallographically distinct blocks and packets during quenching \([3,16-18]\). The confining grain size of austenite is inherited in the martensitic microstructure, and it is a major factor affecting its performance. A lath is a highly dislocated single-crystal martensite plate with an approximate thickness of 0.2–0.5 \(\mu\)m. Adjacent laths are separated by low-angle boundaries with a misorientation angle of about 3–5\(^\circ\). Laths with nearly the same orientation form blocks, and blocks with nearly the same habit plane form packets \([2,3,17,19]\). Grain boundaries such as packet, block, and PAG boundaries can interact with hydrogen in two ways. With high binding energy, they can act as traps that enhance hydrogen embrittlement resistance, or they can act as a conduit for rapid hydrogen diffusion, which in contrast increases hydrogen diffusivity and permeability. In martensitic steels, the predominant hydrogen trapping sites are lath interfaces and PAG boundaries, and typical crack propagation mechanisms of hydrogen embrittlement are intergranular and transgranular quasi-cleavage fractures. The intergranular fracture occurs along the prior austenite grain boundaries, and quasi-cleavage is a transgranular fracture occurring on atypical cleavage planes that show complex, non-uniform features such as river pattern markings, cleavage steps and tear ridges \([3,17,20]\).

In many cases, hydrogen-induced cracking initiates and propagates along PAG boundaries in QT martensitic steels \([9,21-25]\). The influence of PAG size has been extensively studied aiming to suppress intergranular crack propagation by modifying grain size, grain shape, and grain boundary characteristics with somewhat controversial results \([9]\). Grain refinement of QT steels has proven to improve resistance against delayed fracture \([21,26,27]\). Smaller grain size increases the grain boundary area, which reduces the concentrations of the grain boundary embrittling impurity elements via enhanced distribution over a larger area \([3]\). The larger grain boundary area affects also the hydrogen trapping properties and increases the hydrogen absorption capacity \([26]\). The challenge in achieving quantitative understanding lies in widely differing microstructures (retained austenite content, carbides, impurity segregation, grain boundary structure, etc.), which may form during heat treatments conducted for the grain size modification \([9,21]\).

There are studies where the HE effect has been mitigated with an elongated PAG structure through ausforming and tempforming treatments. The reason behind the better HE resistance has been proposed to be transgranular quasi-cleavage crack propagation and high delayed fracture resistance \([8,9,22,23,25,28]\). Based on their elongated PAG morphology, also DQ steels should have a good HE resistance as that of ausformed or tempformed steels. However, there is very little information regarding the effects of the microstructural alignment and PAG shape on the hydrogen-induced fracture in DQ steels, especially when compared to the traditional QT steels. Most studies focus on ausformed/tempformed steels with elongated PAG structures, which are compared to the tempered QT steels with an equiaxed PAG structure \([9,22,23]\). The alloying composition is either the same or the reference material is commercial QT steel with different alloying.

In this study, we investigate the effect of both the size and shape of the PAG structure on hydrogen-induced fracture within the same alloy composition. The original DQ material is austenitized at 860 °C and 960 °C to produce different equiaxed PAG structures. Austenitization at 860 °C produces the same average grain size as DQ, and austenitization at 960 °C produces 4 times larger grain size. No additional tempering treatments are conducted, which enables a new type of comparison of the significance of the PAG structure on HE susceptibility. The influence of the PAG shape and size is investigated with the novel tuning-fork testing (TFT), as well as the traditional electrochemical permeation (EP) tests \([29,30]\). TFT provides data regarding the crack initiation and propagation mechanisms and EP is used to measure hydrogen diffusion coefficient (D), subsurface hydrogen concentration (C_H), and reversible hydrogen trap density (N_T).
2. Experimental procedures

2.1. Test materials

A medium-carbon direct-quenched 500 HBW martensitic steel with main alloying components 0.25C−0.1Si−0.25Mn (wt.%) having an elongated PAG structure was used in the present study to create different PAG morphologies through heat treatments. The original elongated microstructure has been achieved by hot rolling in the non-recrystallization region followed by direct quenching (DQ). To study the effect of PAG morphology with the same chemical composition, the DQ steel plates (300x250x6 mm) were reaustenitized at different temperatures and quenched into a water–oil emulsion, which resulted in an equiaxed PAG structure as presented in Fig. 1. The austenitization temperatures were \( T = 860 \, ^\circ\text{C} \) and \( T = 960 \, ^\circ\text{C} \) with 25 min holding time. All steels have a fully lath-martensitic microstructure with a similar carbide structure as presented in Fig. 2. According to the X-ray diffraction (XRD) measurements, the amount of retained austenite in the original DQ material and the reaustenitized steels was negligible (<1%). Commercial Armco iron was utilized in hydrogen permeation experiments as reference material.

With each steel, tensile tests were conducted with one longitudinally oriented (L) and one transversely oriented (T) specimen with respect to the rolling direction to determine 0.2 % offset yield stress (YS), tensile strength (TS), and total elongation (\( A_{gt} \)). Average hardness values were calculated from 5 measurements/steel and presented with standard deviation (SD) of results. Table 1 summarizes the mechanical properties, average PAG size (\( d_G \)), PAG boundary surface area per unit volume (\( S_{v} \)), and PAG aspect ratio (RD/ND) of each steel grade. Mean PAG sizes were calculated with a novel grain size calculating program [31] from all RD-ND, RD-TD, and TD-ND sections, where RD = rolling direction, ND = normal direction and TD = transverse direction. The program utilizes the mean lineal intercept method and provides a good statistical accuracy with over 200 measured points/material.

The materials have the identical chemical composition, similar tensile strength, and hardness, but the YS of DQ is much higher in comparison to the reaustenitized steels, which suggests that it has also a higher dislocation density. With lower austenitization temperature DQ and A860 have nearly the same \( d_G \) and \( S_v \), which is ideal for studying the effect of PAG shape, and A960 is suitable for studying the effect of grain size of the equiaxed PAG structure. The grain size of A960 is 4 times larger in comparison to that of A860, which subsequently decreases the PAG boundary surface area and supposedly affects the hydrogen trapping/diffusion properties.

The microstructures were studied also with electron backscatter diffraction (EBSD) analysis with a Zeiss Sigma field-emission scanning electron microscope (FESEM). EBSD scans were conducted with 2500× magnification and 0.1 µm step size. Fig. 3 presents the EBSD inverse pole figure (IPF) images and distribution of grain boundary misorientation angles with a marked number fraction of low-angle boundaries with less than 5°. For IPF images, grains with less than 30 indexed points were removed and grain maps were assembled from datasets with 15° grain boundary tolerance for average block size calculations. The average block size was established by calculating the average equivalent circle diameter of all grain polygons. All three test materials have the same average block size of 1.7 µm (DQ = 1.68, A860 = 1.69, A960 = 1.73). Based on the misorientation angle fractions, DQ has 12 % more low-angle boundaries than A860 and 4 % more than A960, indicating that DQ has a finer lath-structure when compared to the reaustenitized ones.

2.2. Tuning-fork testing (TFT)

Tuning-fork test is a novel testing method that has been under development since 2016 [30,32,33]. The motivation was to create a relatively simple but fast testing system, which would not require a tensile test equipment and would allow to rank ultrahigh-strength steels by their HE susceptibility.

Tuning-fork design is based on geometry, which has been utilized in stress corrosion cracking (SCC) testing of aluminium alloys [34]. Because of the high strength of the investigated materials, traditional geometries such as bent-beam [35,36], C-ring [37], U-bend [38,39], and self-loaded tensile specimens [40] were considered complicated due to the risk of spring back, overloading, distortion, misalignment, and stress relaxation with time.

Notched tuning-fork specimens (Fig. 4) were wire electrode discharge machined (WEDM) from 150x50x5 mm billets. Billets were...
machined 0.5 mm/side before WEDM to achieve 5 mm thickness. Two types of DQ steel specimens were studied. DQ L specimens have the longest side parallel to the rolling direction and crack propagation is transverse to it, and DQ T specimens have the longest side transverse to the rolling direction and the crack plane is parallel to it [41]. Therefore, the crack plane is ND-TD with L specimens, and...
with T specimens it is ND-RD. Our previous research has shown that the specimen orientation is not a significant factor for the steels that have an equiaxed PAG structure [30]. Therefore, for the reaustenitized steels, the rolling direction was not considered.

Vickers microhardness measurements were conducted for DQ specimens to understand the microstructural changes caused by WEDM. Near the notch, hardness was 409 HV, and 539 HV in the base material (avg. of 5 measurements). To reveal the microstructure, specimens were etched with 2 % nital and studied with FESEM. Fig. 5 presents the etched notch region with an approximately 4 \( \mu m \) thick layer of a softer microstructure caused by WEDM. Therefore, all the outer specimen surfaces, especially the bottom of the notch, were lightly treated with 600 and 1200 grit emery papers to remove the thin heat-affected zone before testing.

Tuning-fork tests are constant displacement tests under hydrogen charging conditions. The loading of the specimen was performed with a clamp, which has an integrated loadcell system (HBM C9C, 2kN) [30]. By pressing the specimen arms together, a controlled tensile stress concentration is created at the tip of the notch. Stressed specimens were placed in the hydrogen charging environment which induces crack initiation and propagation. The crack propagation stages were monitored through the decrease of load values, i.e., clamp relaxation. The corrosion test cell contains the specimen which acts as the working electrode (WE), a platinum-coated titanium plate as the counter electrode (CE), and a Luggin capillary probe connected to a Hg/Hg2SO4 reference electrode (RE), while the constant potential of \( -1.2 \) V is maintained with a VersaSTAT3 potentiostat. The electrodes were placed in a removable plastic cap, which is positioned on top of the glass cell as presented in Fig. 6. During hydrogen charging, the fresh deaerated electrolyte was pumped to the bottom of the corrosion test cell at a rate of 2 ml/min. The excess electrolyte flows over through an outlet at the top of the cell, which is the key to maintaining the same electrolyte level through all the tests.

A similar hydrogen charging environment as in our previous research (0.1 M H2SO4 + 1 g/l thiourea) was used in the tuning-fork tests, but this time with notched specimens. By utilizing notched specimens, it is possible to initiate only one crack, establish initiation time (\( t_i \)), time-to-fracture (\( t_f \)), and calculate the average crack propagation rate (CPR) by dividing the crack propagation time by the crack length (4.2–4.4 mm). The length of the crack path was 4.5 mm, but the cracks never propagated through the whole specimen, and therefore a small remaining unbroken ligament had to be broken by hand. The length of the ruptured region was measured with a laser microscope for calculation of the average CPR.

Finite element method (FEM) software Abaqus was used to calculate the compressed arm distance required for desired loading conditions. In our previous study, we used elastic stress levels 1/3 TS, 1/2 TS, or 2/3 TS, which were calculated for unnotched specimens [30]. With the notched specimens, the maximum von Mises stress level of 1000 MPa was applied, which corresponded to 1.49 mm arm displacement and 18.51 mm arm distance between the tuning-fork arms. 1000 MPa stress level was calculated for the middle of the notch. Fig. 7 presents the von Mises stress distribution along the notch and Fig. 8 illustrates a clamped specimen with von
Mises stress distribution ahead of the notch tip from the specimen side when stressed at 1000 MPa. The corners of the notch have slightly higher stress in comparison to the middle part meaning that the corners are likely to act as the crack initiation sites, also due to increased effective surface area at the corners (Fig. 7). With 1000 MPa, local stresses do not exceed the materials’ yield strength, i.e., no plastic deformation occurred for any of the test materials, and it was considered to provide the same driving force for the crack initiation within the test matrix.

To analyse the force data, 10 point moving average was applied for the unfiltered data sets, as the unfiltered data (1/s) has a lot of random fluctuations. A moving point average was selected due to its simplicity and because it does not alter the observed signal form. $t_i$ and $t_f$ were determined using the same approach as in our previous research [30], i.e., by the selection of the limiting angle. The limiting angle stands for the angle between the start/end line and the force data. Because of some force fluctuation, the start/end lines are calculated from the average of selected data points. In these tests, the average of the first 500 force data points was used to calculate the start line and the average of the last 50 to calculate the value for the end line, respectively. Fig. 9 presents an example of unfiltered
Fig. 8. Von Mises stress distribution of the notched tuning-fork specimen when loaded up to 1000 MPa.

Fig. 9. An example of filtered and unfiltered t-F curves with marked start and end lines. Initiation time ($t_i$) and time-to-fracture ($t_f$) are determined with the $5^\circ$ limiting angle.

Fig. 10. Hydrogen permeation test set-up.
and filtered time-force (t–F) data with marked points for $t_i$ and $t_f$, which were determined with the selected 5° limiting angle.

For each test material, 5–7 tuning-fork tests were conducted to determine $t_i$, $t_f$, average CPR, and maximum CPR. For each group, the interquartile rule was applied to find outliers. In addition to the regular tuning-fork tests, one interrupted test was conducted for each material to study the short crack initiation at the tip of the notch. The interrupted tests were terminated after approximately 5–10 N drop in the force values. Additional interrupted tests with different charging times were conducted with DQ T specimens for macroscopic examination of the fracture surfaces.

### 2.3. Hydrogen permeation

Electrochemical permeation (EP) tests were performed using the standard Devanathan-Stachurski method to calculate the hydrogen diffusion coefficient (D), subsurface hydrogen concentration ($C_{H}$), and reversible trapping site density ($N_T$). The Devanathan-Stachurski cell is a two-compartment electrolytic permeability cell with hydrogen entry (left) and hydrogen exit (right) sides, where the steel specimen is clamped between the cells acting as WE [29,42]. Fig. 10 presents the test set-up utilized in the hydrogen permeation experiments. Both cells were filled with the same 0.1 M NaOH electrolyte with SCE acting as RE, and platinum-coated titanium mesh acting as CE. On the left side, the deaerated electrolyte was pumped to the bottom of the cell at a rate of 3 ml/min. The excess electrolyte flows through an outlet at the top of the cell maintaining an approximately 300 ml volume. On the right side, N2 bubbling was conducted with a separate inlet. During the test, two separate GillAC potentiostats were used to apply the constant potential on both sides of the cells.

Before testing, both sides of the steel specimen (40x35x1 mm) were mechanically polished with 3 µm diamond suspension to achieve a mirror surface. The exit side of the specimen was then electroplated with palladium (Pd) using a commercial palladium bath containing 6 g/l Pd to get an approximately 1 µm coating thickness [43]. After electroplating, the uncoated side was repolished, and the hydrogen permeation test started.

Hydrogen charging was conducted with 0.1 M NaOH solution, which is different from the tuning-fork tests. With 0.1 M NaOH electrolyte, less hydrogen is produced, and it makes the permeation easier to control. At the beginning of each permeation test, a steel specimen was clamped between the two cells so that the palladium-coated side was on the hydrogen exit side. The hydrogen exit cell was filled with deaerated electrolyte, and a constant anodic potential of 0.3 V was applied. Meanwhile, the hydrogen entry side was bubbled with N2 to maintain inert conditions and prevent specimen oxidation. Once the background current decreased to 0.3–0.1 µA/cm², the hydrogen entry cell was filled with deaerated electrolyte, and a constant potential of hydrogen pre-charging with −1.2 V was started. Pre-charging was maintained for 12 h, which was assessed as sufficient in filling irreversible hydrogen traps. During hydrogen charging, the oxidation/permeation current on the exit side of the cell is recorded as a function of time until it reached a steady state.

After pre-charging and achieving a steady-state permeation current, the successive partial decay and build-up transients were measured by lowering the cathodic potential to −1.1 V and then increasing back to −1.2 V two times. The applied potential for each decay and build-up curve was held for 4 h. Since the reversible traps were filled, the obtained 4 transients are diffusion-controlled and can be used for the calculation of D and $C_{H}$. At the end of the final build-up transition, the cathodic hydrogen charging is switched off and the exit side is polarized to 0.3 V for 2 h until complete decay. When the anodic potential is applied on the entry side, hydrogen is released from traps and therefore the last transient can be used for the characterization of reversibly trapped hydrogen [44]. In the case of Armco iron, 12 h pre-charging was conducted, followed by 2 min transients and 4 min complete decay curve.

One EP measurement can be divided into 3 steps, passivation on the exit side and hydrogen pre-charging (1st step), measuring partial decay and build-up curves (2nd step) and complete decay (3rd step). All the steps during the EP are summarized in Table 2 and an example of the permeation curve of DQ steel with all measured transients is presented in Fig. 11.

#### 2.3.1. Hydrogen diffusivity and solubility

A refined successive transient method was applied to calculate the hydrogen diffusivity and solubility, in which the permeation transients can be expressed by the following equations [20,44]:

**Build-up:**

<table>
<thead>
<tr>
<th>Step</th>
<th>Entry side</th>
<th>Exit side</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step 1</strong></td>
<td>Passivation</td>
<td>N₂ bubbling (inert environment)</td>
</tr>
<tr>
<td><strong>Pre-charging</strong></td>
<td>Introduction of electrolyte</td>
<td>Apply: $E = 0.3$ V, until permeation current is less than 0.3 µA/cm² (1–2 h)</td>
</tr>
<tr>
<td><strong>Step 2</strong></td>
<td>Decay 1 &amp; 2</td>
<td>$E = -1.2$ V (12 h), up to steady state</td>
</tr>
<tr>
<td></td>
<td>$E = -1.1$ V, (2 h/step) down to steady state</td>
<td>$E = 0.3$ V, up to steady state</td>
</tr>
<tr>
<td><strong>Build-up 1 &amp; 2</strong></td>
<td>$E = -1.2$ V (2 h/step), up to steady state</td>
<td>$E = 0.3$ V, down to steady state</td>
</tr>
<tr>
<td><strong>Step 3</strong></td>
<td>Complete decay</td>
<td>$E = 0.3$ V (4 h), down to total discharge</td>
</tr>
<tr>
<td></td>
<td>$E = 0.3$ V, down to total discharge</td>
<td>$E = 0.3$ V, down to total discharge</td>
</tr>
</tbody>
</table>
where $D$ = hydrogen diffusion coefficient, $L$ = specimen thickness, $i_p$ = measured permeation rate at time $t$, $i_0^p$ = initial hydrogen permeation rate ($t = 0$), $i_{\infty}^p$ = new steady-state permeation rate ($t \to \infty$) and $n = 2$. Mathematical curve fitting (GUI tool) was used to fit Eq. (1) to build-up permeation curves and Eq. (2) to decay permeation curves. Based on the $D$ value, the subsurface hydrogen concentration ($CH$) at the entry cell during charging was calculated with the following equation [20, 44]:

$$CH = \frac{i_{\infty}^p L}{FD}$$

where $i_{\infty}$ stands for steady-state permeation current, $L$ for specimen thickness and $F$ is Faraday constant.

2.3.2. Hydrogen trapping

Complete decay is sensitive to hydrogen detrapping, and the desorption rate of hydrogen consists of diffusible and reversibly trapped hydrogen. The density of reversible hydrogen traps ($N_T$) can be evaluated by calculating the area difference ($A$) between the experimental total decay transient and the theoretical decay curve with no traps [13–15, 44]. The theoretical curve can be reconstructed based on the average $D$ values, which are determined from the diffusion-controlled partial decay and build-up transients (see Table 2, Step 2). The simplest case is the assumption that there is only one type of hydrogen trap, and each trap holds one hydrogen atom. $N_T$ can then be calculated according to Eq. (4) [15].

$$N_T = \frac{2A \cdot 6.24 \cdot 10^{18}}{L}$$

where $N_T$ is the reversible hydrogen trap density per unit volume (sites/cm$^3$), $A$ = area difference between the complete decay and theoretical permeation transients (As/cm$^2$), $L$ = specimen thickness (cm) and $6.24 \cdot 10^{18}$ is the number of hydrogen traps ($1C = 1 \text{As} = 6.24 \cdot 10^{18}$ e).

2.4. Microscopy

A stereo-microscope was used for the macroscopic study of the fracture surfaces, a laser-microscope was used to measure the remaining unbroken ligaments of the fracture surfaces and to study the etched PAG structure, and FESEM was used for microscopic examination of the fracture surfaces and to study the PAG substructure. Metallographic investigations were conducted with an optical microscope and a Zeiss Sigma field-emission scanning electron microscope (FESEM) equipped with an electron backscatter diffraction (EBSD) camera. EBSD scans were conducted from the approximately mid thickness of the steel plates using an accelerating voltage of 15 kV and a working distance of 15 mm. All EBSD data were post-processed with MTEX, which is a MATLAB toolbox for texture and crystallography analysis [45].

The microstructures were studied with hot-mounted, ground, and polished specimens. The martensitic microstructure was revealed with 2% nital etching, PAG structure with a picric acid solution (1.4 g picric acid + 100 ml distilled water + 1 ml wetting agent + HCl drops), and EBSD specimens were unetched. For fractographic analysis, fracture surfaces were cut and chemically cleaned with a specific solution (50 ml HCl, 450 ml distilled water, and 15 g hexamethylene-tetramine) followed by a 10 min plasma cleaning (Plasmalab 80 Plus) to remove the corrosion products. After interrupted tests, the notched region was studied with both a laser.
microscope and FESEM. First, the specimens were polished for EBSD analysis and studied with FESEM + EBSD. Afterwards, they were repolished and etched to reveal the PAG boundaries and studied with the laser microscope. For IPF images of interrupted tests, 5000x magnification and 0.07 μm step size were used with DQ and A860 materials, and 2500x magnification and 0.1 μm step size for A960 steel. Grain maps were assembled from datasets with 5° grain boundary tolerance. Fracture surfaces represent the ND-RD/TD crack plane and interrupted tests show the RD-TD plane, depending on the specimen orientation.

3. Experimental results and discussion

3.1. TFT

Recorded force–time data from the tuning-fork tests with steels DQ (L and T orientations), A860, and A960 are presented in Fig. 12. For all the steels, the initial force is in the range of 68–81 N with good repeatability between the curves of each group. The curve shape is similar for both DQ directions, with crack initiation (plateau) and crack propagation region, which shows gradually decreasing force values. For the reaustenitized steels, the crack propagation stage ends abruptly, which shortens their time-to-fracture in comparison to DQ.

The obtained \( t_i \) and \( t_f \) values are presented in Fig. 13, and the average and maximum CPR results are presented in Fig. 14. For \( t_i \), no statistical differences are observed between the steels and different directions (\( p = 0.05 \)), which correlates with the fact that the same driving force, i.e., arm distance, was applied for all the tests. Yet, significant differences are obtained in the crack propagation times, which allows utilization of CPR values for hydrogen embrittlement performance evaluation.

DQ L has the slowest average CPR of the compared materials and therefore the best performance. In contrast, DQ T and both reaustenitized steels with equiaxed PAG structures have faster CPR in comparison to that of DQ L. All data is normally distributed, and the results are significantly different with exception of DQ T and A960 (\( p = 0.05 \)), which also have the same average CPR. Max CPR values of DQ (both directions) are 3–4 times lower in comparison to the reaustenitized steels indicating a significant effect of the PAG morphology and/or growth type.

Considering only the equiaxed PAG structures of A860 and A960 with different PAG sizes, A860 has a significantly faster CPR in comparison to A960, indicating better performance of larger PAGs. However, A860 has slightly lower start force values in comparison to other steels. The difference is distinctly grouped for A860; therefore, it is not a statistical error but is probably related to the microstructure. Better comparison could be achieved in the future by selecting a specific force value instead of distance, such as 75 N.

The effect of PAG refinement on hydrogen resistance is a controversial topic in literature: in steels prone to intergranular cracking, i.e., quenched and tempered steels with equiaxed PAGs, PAG refinement has improved the resistance to delayed fracture [21,26,27]. Enhanced resistance to hydrogen-induced cracking has been reported in medium-carbon martensitic steels with higher hydrogen absorption capacity [26]. PAG refinement, and therefore larger grain boundary surface area has improved HE resistance also in 8Ni-0.1C martensitic steel by reducing the area fraction of intergranular cracking [27]. Contradicting the above mentioned findings, hydrogen-induced fracture resistance has also been improved with larger PAG size due to higher threshold stress intensity and slower crack propagation [24,46,47]. Due to different start force values of A860 in comparison to other steels, the effect of equiaxed PAG size on CPR is not fully transparent, and more investigations are required to confirm the CPR trend with, e.g., intermediate PAG size of ~25 μm. CPR results of A860 can be affected by lower initial force values as well as hydrogen diffusion and crack propagation mechanisms, which are further discussed in the following chapters.

There are significant differences in the DQ L and T results, but they cannot be explained by the differences in hydrogen diffusion as it is the same material. Although permeation test orientation could have a minor role, this L and T direction dependence could not be
Fig. 13. Initiation time ($t_i$) and time-to-fracture ($t_f$) results of investigated materials stressed at 1000 MPa.

Fig. 14. Average CPR and maximum CPR results of investigated materials stressed at 1000 MPa.

Fig. 15. PAG structure of crack propagation planes of DQ L and T specimens.
tested here. The main difference between L and T orientations is the PAG size and shape in the crack plane. L has a smaller average $d_G$ in comparison to T and because of the PAG elongation, there are fewer grain boundaries to be crossed during the crack propagation. Fig. 15 illustrates how the PAG size and shape differ in the crack plane of differently oriented DQ specimens. Smaller PAG size combined with more grain boundaries on the crack path can contribute to the slower CPR of DQ L. The results indicate that the direction of crack propagation in terms of the elongated PAG structure can significantly affect CPR and subsequently HE resistance. Depending on the direction and PAG size, HE resistance can be better in comparison to the equiaxed PAG structure with the same alloying.

3.1.1. Fractography

To understand the crack initiation and propagation mechanisms, interrupted tests with different charging times were conducted with DQ T. The results are given in Fig. 16, where all $t-F$ curves are presented with a side view of the cracked specimen and a corresponding macroscopic image of the fracture surface. In the interrupted tests, the utilized electrolyte discolours the existing fracture surface of the propagated crack. The crack propagates slightly faster from the corners than in the middle of the notch (Fig. 16), which is explained by increased effective surface area for hydrogen diffusion at the corners under tensile stresses (see Fig. 7).

The crack propagation occurs from three different directions that coalesce and cause the abrupt fracture and change in the force values for some of the tests. Microscopic examination of the fracture surfaces shows that in the middle of the specimen usually a ductile fracture area is present as shown in Fig. 17. Crack coalescence from three directions leads to a fast crack growth of the equiaxed PAG structure (see Fig. 12 for A860 and A960) and it is the main event affecting the max CPR results. Max CPR values are significantly lower for DQ steel, which did not show abrupt force drops. In all tests, a small ductile region exists in the middle of the specimen and in the remaining unbroken ligament at the end of the crack path, which is broken by hand.

Fig. 18 presents general and detailed views of fracture surfaces of the investigated materials. The fractographic analysis demonstrates two different PAG shape-dependent hydrogen-induced cracking mechanisms. For DQ with the elongated PAG structure, crack propagation is mainly transgranular quasi-cleavage in both directions. It has been reported that in steels rolled in the non-recrystallization region (elongated PAGs), large stress does not act at the boundaries if applied parallel to the elongated grains. This leads to occurrence of quasi-cleavage cracking, which is observed for the DQ L, where applied stress is parallel to the elongated PAGs. [22].

For both reaustenitized steels with the equiaxed PAG structures, crack propagation is partly intergranular. Based on the fracture surface appearance, higher CPR of A860 and A960 in comparison to DQ L is attributed to the change in the crack propagation from transgranular quasi-cleavage to intergranular fracture. It must be noted that DQ (L and T) has the smallest average $d_G$ in the crack plane, which can affect the crack propagation rate and mechanism. Furthermore, intergranular crack propagation can result from grain boundary impurity segregation. Despite that the nominal content of grain boundary embrittling impurity elements is the same for all the studied steels due to the same alloying, different grain growth mechanism in stress-free high-temperature reaustenitization (A860 and A960) can locally accumulate impurities to the grain boundaries.

For the equiaxed PAG structures, an intergranular fracture is recognized based on the three-dimensional character of the grains with separated grain boundary surfaces and faceted morphology. For an elongated, asymmetrical PAG structure, the intergranular crack path does not appear favourable in a similar manner. However, DQ T fracture surfaces exhibit some flat features, which do not appear to be pure cleavage, either. These are marked with white arrows in Fig. 15. Based on their size, shape, and topography, these
features appear to be separated grain boundary surfaces. A faster CPR of DQ T specimens in comparison to DQ L can so be explained with some additional intergranular crack propagation and/or less grain boundaries on the crack path.

The notch area is studied separately with interrupted tests. The results are presented in Fig. 19, which combines laser-microscopy and EBSD images (etched PAGs and IPF) of the crack initiation region and further crack propagation. In the IPF images, the PAG boundaries are marked with white dash lines. Crack initiation occurs most likely at the PAG boundary in all cases. As indicated by the fracture surfaces and the notch area, the equiaxed PAG structure leads to a mixture of intergranular and transgranular fracture, crack branching, and the elongated PAG structure leads mainly to the straight propagating transgranular (quasi-cleavage) fracture.

3.1.2. TFT assessment

Original query for TFT came from the industry, wishing for simpler and readily made available test method compared to fracture mechanical testing. This is pursued and achieved in this study. In the current state, TFT provides a variety of parameters in a matter of hours (t_i, t_f, CPR), which are important in understanding hydrogen-induced cracking. The obtained results are further supported and explained by fractography analysis. The testing method has good repeatability, and its capability and efficiency in ranking steels is demonstrated with ultrahigh-strength steels. However, A860 steel had slightly deviating initial force values, which raises a question regarding sensibility of clamping. Therefore, the development work will be continued and there are several improvements that can be made to clamping arrangement and to results analysis, which can broaden utilization of TFT.

With current geometry and clamping system, only very small displacements can be applied to assure elastic stress level. Lower elastic stress requires less displacement and makes firm clamping difficult. The stress intensity factor of the notch could be decreased by widening of the notch angle up to 170°, which can be achieved with wire cutting and it would double the elastic displacement range. Bigger displacement range would allow comparison of different elastic stress levels and studying of steels with lower YS. Also, the clamping system can be modified to provide improved measurement for displacement e.g., with differential screw system and a more sensitive loadcell. With less fluctuating force values, a specific force value could be chosen for steel comparison instead of displacement. On the other hand, research can also be conducted with small plastic region [48].

Additional interrupted tests could be conducted to study the critical crack length of steels, too. Samples can be taken out of the hydrogen charging environment after the crack has propagated, e.g., 25 % or 50 %, and then be kept in air to see if the crack propagation will continue. This would provide information regarding delayed cracking susceptibility and refer to industrial processes where hydrogen is present in cycles. Tuning-fork tests could be also conducted in different hydrogen charging environments or as a simple immersion test.

In the future, the developed TFT method will benefit from comparison with traditional HE testing methods such as constant load (CL), constant strain rate test (CERT), and 3/4 point bending under continuous hydrogen charging. The comparison will be most efficient with notched specimens and similar hydrogen charging environment. From the mentioned testing methods, 3/4 point bending has the most comparable stress state in comparison to the TFT.

3.2. Hydrogen permeation

The obtained decay and build-up curves for each steel and their fitted curves are presented in Fig. 20. The experimental transients are repeatable and reproducible, giving approximately the same D value for all 4 transients/material. The overlapping of experimental and fitted curves indicates that the permeation of hydrogen is diffusion-controlled [44].

Fig. 21 presents the differences in diffusion coefficients of the studied materials and Table 3 contains the detailed values of obtained D and C_H and N_T data. As indicated in Table 3, the subsurface hydrogen concentration is higher with more negative hydrogen charging potential, with Armco having the lowest C_H. Because the main interest is the effect of PAG structure on hydrogen embrittlement, the D results are plotted with PAG boundary surface area per unit volume (S_PAG) as the second y-axis in Fig. 21. Armco iron was selected as the...
Fig. 18. General (left column) and detailed views (right column) of fracture surfaces of investigated steel grades. White arrows mark suspected intergranular features of DQ T specimens.
reference material because it has been widely studied, and it can be used to evaluate the reliability of the conducted permeation experiments. The average D of Armco iron is $3.4 \times 10^{-5}$ cm$^2$/s, which is in the same order of magnitude as the reported values from similar test conditions [44,49]. Hydrogen diffusion is significantly faster in Armco iron than in the given steels as it has a softer and simpler ferritic microstructure with fewer hydrogen traps. From the studied high-strength steels, DQ has the slowest $D = 4.7 \times 10^{-7}$ cm$^2$/s, which is significantly slower ($p = 0.05$) than A860 and A960 with an average $D$ of $5.4 \times 10^{-7}$ cm$^2$/s and $5.5 \times 10^{-7}$ cm$^2$/s, respectively. Subsurface hydrogen concentration is higher with more negative hydrogen charging potential with Armco having the lowest $C_H$ (Table 3). No correlation is observed between D and $S_V$, indicating that PAGs are not effective diffusion paths for hydrogen. $D$ has been reported to be in the range of $\sim 1 \times 10^{-6}$ to $8 \times 10^{-7}$ cm$^2$/s [50,51] in a similar environment for predominantly martensitic steels with similar mechanical properties as the steels investigated here. This similarity validates the effect of PAG structures further.

Diffusion coefficient tends to decrease with the increased mechanical strength of martensite. Martensite has the highest density of dislocations and grain boundary interfaces among bcc microstructures which lead to greater hydrogen trapping [50,51]. The microstructure (excluding PAG size and morphology), and the mechanical properties such as tensile strength and hardness are relatively similar within this study. Therefore, the main difference is the PAG structure. Minor variation can also be due to smaller differences in the dislocation density (higher YS) as well as sub-PAG grain size that originate from different manufacturing methods, e.g., lath structure. DQ has the last rolling stage happening below the recrystallization finish temperature, where the austenite grains are elongated, which introduces a lot of crystallographic discontinuities inside the grains. These discontinuities are potential nucleation sites in following fcc-bcc transformation, leading to finer martensitic microstructure. Therefore, the phase transformation from the deformed austenite (DQ) produces a finer grain size than that from the strain-free austenite (A860 and A960) [52,53]. Consequently, DQ steel should have both more discontinuous diffusion paths and traps for hydrogen than the reaustenitized and quenched martensite, which explains the slower diffusion coefficient of DQ.

Based on the average D values (see Table 3/Fig. 21), the theoretical decay curves are determined for the total discharge transient (Step 3). Since D was calculated from 2 h/min transients, the same time was utilized in calculations of the area difference between the theoretical and measured curves (Fig. 22), which was used to calculate $N_T$. Similarly, $S_V$ is used as the second y-axis to present the
The correlation between NT and the PAG structure (Fig. 21). The time scale in Fig. 22 is logarithmic due to the completely different total discharge times of Armco iron (2 min) and steels (2 h). The NT of Armco iron is $4.1 \times 10^{14}$ sites/cm$^3$, which is as expected, a few orders smaller in comparison to steels. For the studied steels, NT values are in the range of $2.8–3.5 \times 10^{16}$ sites/cm$^3$. In theory, diffusion is slowed down by trapping, weak and strong traps, and the number of traps should be higher with slower diffusion. In our case, NT results are approximately the same for DQ and A860, but A960 has the highest number of weak traps. When compared with SV, the number of weak traps increases with the lower amount of PAG boundaries. This can be interpreted to that PAG boundaries are in this case acting as strong traps. When SV is smaller, there are fewer PAG boundaries and more steel matrix and other interfaces acting as reversible traps. However, the differences in NT between the materials are still relatively small, which reflects the similarity of the microstructures. The effect of NT cannot be quantified within the present study, and it requires further investigations, which should

Fig. 20. Normalized decay ($-1.2 - -1.1$ V$\text{SCE}$) and build-up ($-1.1 - -1.2$ V$\text{SCE}$) transients with fitted curves. Note the different time scales of Armco iron and steels.

Fig. 21. Diffusion coefficients for Armco, DQ, A860 and A960.
also consider the effect of irreversible trapping.

There is a direct correlation between the obtained average \( D \) results and CPR values. A slower hydrogen diffusion rate leads to a slower CPR in the case of DQ, while A860 and A960 have higher CPR and higher \( D \). However, there is no correlation between the PAG structure and hydrogen diffusion. Generally, PAG boundaries can act as traps or/and as a conduit for hydrogen diffusion, which increases hydrogen diffusivity and permeability. In our case, the 4 times larger PAG size of A960 in comparison to that of A860 did not affect the average \( D \). A860 and A960 have very different \( S_v \) but similar \( D \), which indicates that PAG boundaries cannot be the predominant diffusion paths. This also explains why crack propagation was only partially intergranular for these steels. DQ and A860 have similar \( S_v \) but different \( D \), which also suggests that hydrogen diffusion is affected more by other microstructural features and interfaces than PAG boundaries. If hydrogen diffusion is not dominated by the PAG structure, different crack propagation mechanisms can be then attributed to the different PAG shapes, and possibly also to the PAG growth mechanism. The elongated PAG structure is irregular with larger dihedral angle in the transverse direction in comparison to equiaxed PAGs. Therefore, intergranular crack propagation transverse to elongated structure (DQ L) requires more deflections than in equiaxed structure. However, intergranular propagation longitudinal to elongated PAGs does not require as many deflections, and some intergranular cracking occurs. The geometrical structure of the grain boundaries is considered to suppress intergranular crack propagation in transverse direction, while the equiaxed grain structure is more sensitive to intergranular crack propagation.

4. Conclusions

This study investigated the effects of prior austenite grain (PAG) structure on the hydrogen embrittlement susceptibility of three as-quenched martensitic steels. The original material is 500 HBW direct-quenched (DQ) steel with an elongated PAG structure, which is modified by austenitization at 860 °C (A860) and 960 °C (A960) to produce equiaxed PAG structures with different grain sizes within the same alloy composition.

The effects of PAG shape and size on hydrogen embrittlement were investigated with the novel tuning-fork test to determine the average crack propagation rate (CPR), and to study crack initiation and growth mechanisms under elastic constant displacement. Anisotropic DQ was tested in both longitudinal and transverse orientations. The mechanical test results were complemented with
traditional hydrogen permeation testing to obtain a further understanding of hydrogen diffusion and trapping in the studied steels. The following conclusions were drawn from this study:

1. Novel tuning-fork test can be utilized in ranking of HE susceptibility of ultrahigh-strength. Each test provides initiation time, time-to-fracture, and average and maximum crack propagation rates in a matter of hours, which can be corroborated with fractography analysis. Test setup will still benefit from further development to achieve wider elastic stress range for displacement and less fluctuation in force values.

2. DQ steel with elongated PAG structure produces different CPR results depending on the crack propagation direction. Significantly slower CPR, and therefore enhanced HE resistance in comparison to the equiaxed PAG structures, is achieved when crack propagation is transverse to the rolling direction. If crack propagation is parallel to the rolling direction, CPR is similar as for the equiaxed PAG structure.

3. Crack propagation changes from transgranular to intergranular depending on the PAG shape. Elongated direct-quenched PAG structure leads to a slower transgranular quasi-cleavage fracture, and equiaxed PAG structure to a faster, partly intergranular fracture, which can be linked to the geometrical shape of the grains. Depending on the crack propagation direction within the equiaxed PAG structure, some intergranular cracking occurs also in the crack propagation direction in individual elongated PAGs parallel to the rolling direction, accelerating its CPR.

4. There is a direct correlation between CPR and hydrogen diffusion coefficient (D) but no correlation between the S values and D. Slower hydrogen diffusion rate leads to slower CPR values but differences in S values have no systematic effect on D. DQ and A860 have similar S values but very different D, while A860 and A960 have a fourfold difference in PAG size and S values but nearly identical D. Therefore, PAG boundaries are not acting as the predominant diffusion paths, but hydrogen diffusion is affected more by other microstructural features and interfaces.

CRediT authorship contribution statement

Renata Latypova: Conceptualization, Data curation, Writing – original draft, Writing – review & editing, Visualization, Investigation, Validation, Formal analysis, Methodology. Oskari Seppälä: Writing – review & editing, Methodology, Validation, Software. Tun Tun Nyo: Methodology, Investigation. Timo Kauppi: Methodology, Investigation. Saara Mehtonen: Writing – review & editing, Supervision. Hannu Hänninen: Writing – review & editing, Supervision. Jukka Komi: Supervision, Funding acquisition, Resources. Sakari Pallaspuro: Conceptualization, Writing – review & editing, Validation, Supervision, Funding acquisition.

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.

Data availability

Data will be made available on request.

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