

Characterisation of the Hydrogen Interaction with Duplex and Austenitic Steels

Lisa Claeys

Doctoral dissertation submitted to obtain the academic degrees of Doctor of Materials Engineering (UGent) and Doctor of Engineering Sciences (VUB)

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### Summary

The transition to a hydrogen economy is ongoing. The use of hydrogen will reduce the need for fossil fuels and limit global warming. It order to do so safely, hydrogen-compatible materials should be available. In metals, however, hydrogen is known to cause a degradation of the mechanical properties when present in the microstructure. The degradation mainly manifests itself in a reduction of the metal's ductility. Major research efforts were already performed to reveal the underlying mechanisms of the hydrogen embrittlement phenomenon. A vast amount was devoted to the study of body centered cubic steels including different kinds of high strength steels which were particularly prone to hydrogen-induced degradation. Face centered cubic steels, i.e. austenitic steels, showed improved hydrogen embrittlement resistance compared to body centered cubic steel types due to the lower hydrogen diffusion rate which is one of the key influencing parameters. Nevertheless, austenitic steels were also found to suffer from significant hydrogen-induced degradation. As important candidate materials for hydrogen engines, transportation and storage systems and other applications that come into contact with hydrogen during their life-time, research therefore also focussed on the improvement of the hydrogen embrittlement resistance of austenitic steels. Hence, the aim of this doctoral thesis was to further increase the understanding of the interaction between hydrogen and austenite-containing steel types to be able to proceed to the knowledge-based development of hydrogen-resistant materials.

Chapter 1, 2 and 3 give a general introduction to the research performed in this PhD. In chapter 1, the subject of the dissertation is introduced and the general objectives and outline of the work are given. In chapter 2, a literature review is presented including a part on the deformation mechanisms that are characteristic for austenitic steels, i.e. dislocations processes, deformation twinning and martensitic transformations, and a part on hydrogen embrittlement including both a general description of the phenomenon and a specific literature review on the already published findings regarding the interaction between hydrogen and austenitic steels. In chapter 3, the used methodologies are explained with particular attention for the low hydrogen diffusivity in austenitic steel types.

In the experimental part of this dissertation, three different material types are investigated: duplex stainless steel, austenitic stainless steel (ASS) and twinning-induced plasticity (TWIP) steel. For every material type, two different chapters are presented. The first chapter includes a general characterisation of the studied materials. It also focusses on the introduction of hydrogen and the interaction between hydrogen and the microstructure. The hydrogen solubility and temperature-dependent effective hydrogen on the mechanical properties is investigated. Tensile tests are performed on the materials with and without hydrogen using different experimental conditions. A lot of attention is put to the microstructural characterisation of the tensile tested specimens to compare the active deformation mechanisms and to determine the microstructurally vulnerable locations for damage initiation and propagation.

In chapter 4, the interaction between hydrogen and 2205 duplex stainless steel is investigated. The duplex stainless steel shows alternating bands of austenite and ferrite along the rolling direction with a total austenite phase fraction of 53%. This two-phase material is studied as intermediate step towards the study of fully austenitic steels, starting from the existing knowledge on body centered cubic steels. Upon the introduction of hydrogen via electrochemical methods at room temperature, slip bands are observed in the austenite phase fraction. Due to the combination of high hydrogen concentrations and high internal stresses, dislocations sources become active, despite the absence of an external stress. The equilibrium surface hydrogen concentration is determined through melt extraction and fitting with an analytical solution of Fick's second law for diffusion. Thermal desorption spectroscopy (TDS) data are analysed and fitted with a numerical diffusion model based on Fick's laws. It is proven that for materials characterised by a low hydrogen diffusivity, only hydrogen diffusion could be distinguished from the TDS data since this is the rate-determining step compared to hydrogen detrapping. The temperature-dependent effective hydrogen diffusion coefficient is quantified by the numerical simulation. The value is situated in between the effective hydrogen diffusivity of the ferrite and austenite phase, separately. Hydrogen trapping could be distinguishable for trap activation energies higher than the diffusion activation energy and/or for higher trap densities. A major advantage of the numerical approach developed in this chapter is the ability to analyse materials that were heterogeneously hydrogen charged which is a major advantage when electrochemical charging is applied.

The influence of hydrogen on the mechanical properties of 2205 duplex stainless steel is discussed in chapter 5. Two different charging times are used, both unable to reach a homogeneous hydrogen concentration through the thickness of the specimen due to the low hydrogen diffusion speed. The fracture surface of in-situ hydrogen tested duplex stainless steel shows quasi-cleavage fracture in the hydrogenaffected zone and ductile dimples in the remaining part of the fracture surface as well as on the full fracture surface of the reference specimens tested in air. A critical hydrogen concentration for quasicleavage fracture is obtained by plotting the size of the brittle zone on the hydrogen concentration profile. A change in the active deformation mechanisms is observed in the presence of hydrogen by using electron backscatter diffraction on intermediately interrupted tensile tested specimens. More planar slip is observed as well as the presence of both  $\epsilon$ - and a'-martensite. This effect is explained by the reduction of the stacking fault energy (SFE) by hydrogen and the pinning of edge dislocations. Hydrogen-assisted cracking is studied as well. For the high hydrogen concentrations used in the present work, crack initiation mainly occurs in the austenite phase fraction. The formed martensitic phases are not prone to crack initiation. Crack propagation occurs mainly transgranular through both the austenite and ferrite phase. When the ferrite phase fraction is increased by performing a heat treatment, the hydrogen embrittlement susceptibility is increased due to the increased average hydrogen diffusivity.

The first research on a fully austenitic steel is presented in chapter 6 and 7 for 304L ASS. This steel is metastable at room temperature, i.e. it transforms to a'-martensite under the influence of deformation. In

chapter 6, the influence of pre-deformation on the hydrogen solubility and diffusivity is investigated. This is done using both electrochemical and gaseous hydrogen charging combined with TDS measurements and the numerical model developed in chapter 4. It is found that the presence of a'-martensite decreases the hydrogen solubility and increases the hydrogen diffusivity. An alternative methodology for the determination of the effective hydrogen diffusion coefficient is presented as well, i.e. constant temperature hydrogen desorption experiments. The prerequisite of a homogeneous hydrogen concentration through the thickness is achieved by the high temperature gaseous charging procedure.

In chapter 7, the influence of the crosshead displacement rate on the hydrogen embrittlement sensitivity of 304L ASS is evaluated. The lower the deformation rate, the more hydrogen is able to embrittle the stainless steel type due to the time that is given for hydrogen to diffuse. Due to the metastability of the austenite matrix, the effective hydrogen diffusion coefficient continuously increases during the tensile test increasing its sensitivity to hydrogen embrittlement compared to stable austenitic steels. The martensitic transformations, however, positively influences the ultimate tensile strength and elongation at fracture of 304L ASS. Both the restriction of the adiabatic heating effect and the presence of hydrogen enhance the α'-martensitic transformation. Moreover, ε-martensite is additionally detected which was absent in the air reference tests without hydrogen. When both hydrogen and the temperature effect increase the extent of the martensitic transformations during in-situ testing at high deformation rates, an increase in elongation is noted compared to an air reference. This observation suggests that hydrogen could act as a strengthening interstitial element as well opening opportunities for the development of hydrogen-resistant alloys. Furthermore, it is reported that the hydrogen-affected zone on the fracture surface shows guasi-cleavage characteristics and increases in size with decreased crosshead displacement rate. Finally, applying deformation prior to tensile testing with hydrogen increases the hydrogen embrittlement sensitivity due to the presence of microstructural defects and the increased hydrogen diffusivity.

The second fully austenitic steel that is studied is twinning-induced plasticity steel. Unlike 304L ASS that shows martensitic transformations, this steel is prone to mechanical twinning under the influence of deformation. Three different TWIP steel compositions are studied: Fe-18Mn-0.6C, Fe-18Mn-0.6C-1.5Al and Fe-24.5Mn-0.6C TWIP steel. The addition of aluminium is reported to be beneficial in increasing the resistance to hydrogen in literature. The mechanism is, however, still under debate. One of the possible explanations was linked to the increase in the SFE with the addition of aluminium. To further clarify the effect of the SFE, a TWIP steel with a similar SFE is created by increasing the manganese fraction. The SFE is evaluated based on an established thermodynamic regular solution model for high-manganese steels. In chapter 8, the differences in hydrogen solubility and diffusivity between the TWIP steels are elucidated. The addition of aluminium results in an increase in the hydrogen solubility and a slight decrease of the hydrogen diffusivity. The addition of manganese results in an increase of the hydrogen solubility as well. The hydrogen diffusivity is, however, increased in the presence of manganese.

The influence of hydrogen on the mechanical properties of the three TWIP steels is investigated in chapter 9. Although the hydrogen concentration increases with the addition of aluminium, the beneficial effect on the ductility in the presence of hydrogen is confirmed when comparing the relative loss in elongation at fracture. The addition of manganese is, however, detrimental for the hydrogen embrittlement sensitivity, despite the similar SFE compared to the Al-added TWIP steel. The reason for the difference is twofold. First, aluminium decreases the hydrogen diffusivity while manganese significantly increases it. Second, aluminium increases the grain boundary cohesive strength leading to a higher resistance to crack initiation and a fracture surface mainly characterised by quasi-cleavage features. In contradiction, manganese decreases the grain boundary cohesive strength which caused abundant crack initiation and clear intergranular fracture surfaces. The critical hydrogen concentration is believed to be altered by the difference in dominant fracture mechanism which is clearly advantageous for the Al-added TWIP steel. For all three alloys, the reduction in SFE by hydrogen is confirmed. Both the Al-added TWIP steel and the Fe-24.5Mn-0.6C TWIP steel show a higher twin fraction and the Fe-18Mn-0.6C undergoes ε-martensitic transformations in the presence of hydrogen.

### Samenvatting

De transitie naar een waterstofeconomie is volop bezig. Gebruik van waterstof kan de nood aan fossiele brandstoffen verminderen en kan de opwarming van de aarde vertragen. Voor een veilige transitie moeten uiteraard materialen beschikbaar zijn die compatibel zijn met waterstof. Het is echter geweten dat waterstof de mechanische eigenschappen van metalen kan aantasten wanneer het aanwezig is in de microstructuur. De degradatie uit zich vooral als een verlaging van de ductiliteit van het metaal. Grote inspanningen werden reeds geleverd om het onderliggende mechanisme van deze waterstofverbrossing te achterhalen. Een groot deel daarvan werd gewijd aan kubisch ruimtelijk gecentreerde staalsoorten waaronder verschillende hoogsterkte staalsoorten. Deze laatste werden erg gevoelig bevonden aan waterstofgeïnduceerde degradatie. Kubisch vlak-gecentreerde of austenitische stalen vertonen een hogere resistentie tegenover waterstofverbrossing in vergelijking met de kubisch ruimtelijk gecentreerde stalen door hun intrinsiek lagere waterstofdiffusiesnelheid, een belangrijke invloedsfactor bij waterstofverbrossing. Austenitische stalen zijn echter ook gevoelig voor waterstofgeïnduceerde degradatie. Aangezien austenitische stalen belangrijke kandidaat materialen zijn voor waterstofmotoren, transport en opslag systemen en andere toepassingen die in contact komen met waterstof tijdens gebruik, werd er daarom ook voor austenitische stalen gefocust op onderzoek naar de verbetering van de weerstand tegen waterstofverbrossing. Het doel van dit doctoraatsonderzoek is dan ook om het begrip rond de interactie tussen waterstof en austenitische staalsoorten verder te vergroten zodat waterstofresistente materialen kunnen gemaakt worden op basis van vergaarde kennis over de mechanismen.

In hoofdstuk 1, 2 en 3 wordt een algemene inleiding gegeven tot het doctoraatsonderzoek. In hoofdstuk 1 wordt het onderwerp ingeleid en worden de doelstellingen en opbouw van het doctoraat voorgesteld. De literatuurstudie in hoofdstuk 2 bevat een deel over de vervormingsmechanismen die karakteristiek zijn voor austenitische stalen (dislocatie processen, vervormingsgeïnduceerde tweelingvorming en martensitische transformaties) en een deel over waterstofverbrossing waarbij zowel een algemene beschrijving wordt gegeven als een meer gedetailleerde literatuurstudie van de reeds gepubliceerde bevindingen omtrent de interactie tussen waterstof en austenitische stalen. Tenslotte worden in hoofdstuk 3 de gebruikte methodologieën voorgesteld met bijzondere aandacht voor de trage waterstofdiffusie in austenitische stalen.

In de experimentele sectie worden drie verschillende materiaaltypes onderzocht: duplex roestvast staal (RVS), austenitisch roestvast staal en tweeling-geïnduceerde plasticiteit (TWIP) stalen. De studie van de verschillende materiaalsoorten wordt telkens verdeeld over twee hoofdstukken. Het eerste hoofdstuk bevat steeds aan algemene karakterisering van de materialen. Daarnaast ligt de nadruk in het eerste hoofdstuk ook op de introductie van waterstof en de interactie van waterstof met de microstructuur. De oplosbaarheid en temperatuur afhankelijke gemiddelde waterstofdiffusiecoëfficiënt worden berekend voor verschillende materiaalcondities. In het tweede hoofdstuk wordt de invloed van waterstof op de

mechanische eigenschappen onderzocht door middel van trektesten met en zonder waterstof in verschillende experimentele condities. Er wordt vooral aandacht besteed aan de microstructurele karakterisering van de getrokken stalen ter vergelijking van de actieve vervormingsmechanismen en om de microstructureel kwetsbare plaatsen voor scheurinitiatie vast te stellen.

In hoofdstuk 4 wordt de interactie tussen waterstof en 2205 duplex RVS onderzocht. Het staal vertoont alternerende banden van austeniet en ferriet evenwijdig georiënteerd met de walsrichting en bevat een austenietfractie van 53%. Dit tweefasig materiaal dient als tussenstap naar volledig austenitische materialen startende vanuit de huidige kennis rond kubisch ruimtelijk gecentreerde staalsoorten. Wanneer waterstof in het materiaal geïntroduceerd wordt door elektrochemische methodes op kamertemperatuur, vormden zich slipbanden in het austeniet. Door een combinatie van de hoge waterstofconcentratie en interne spanningen worden dislocatiebronnen actief, hoewel geen externe spanning werd aangebracht. De evenwicht oppervlakteconcentratie aan waterstof wordt bepaald door de stalen te smelten. Hierna wordt een analytische oplossing van de tweede diffusiewet van Fick gefit aan de data. Thermische desorptie spectroscopie (TDS) data worden geanalyseerd en gefit met een numeriek diffusiemodel op basis van de wetten van Fick. Voor materialen die gekenmerkt worden door trage waterstofdiffusie werd bewezen dat enkel deze diffusie kan onderscheiden worden in de TDS data aangezien dit de snelheidsbepalende stap in vergelijking met waterstof detrapping. De temperatuursafhankelijke waterstofdiffusiecoëfficiënt wordt bepaald via de numerieke simulatie. De waarde bevindt zich tussen de afzonderlijke waarden van een ferriet- en een austenietfase. Mogelijks kan waterstof trapping onderscheiden worden bij desorptie activatie-energieën die hoger zijn dan de diffusie activatie-energie en/of bij hoge trap dichtheden. Het grote voordeel van de numerieke analysemethode die werd ontwikkeld in dit hoofdstuk is de mogelijkheid om materialen te analyseren die een heterogene waterstofconcentratie bevatten. Dit is vooral een voordeel wanneer elektrochemische oplaadmethodes gebruikt worden.

De invloed van waterstof op de mechanische eigenschappen van 2205 duplex RVS wordt besproken in hoofdstuk 5. Twee verschillende oplaadtijden worden gebruikt. Beide tijden leiden echter niet tot een homogene waterstofconcentratie doorheen de dikte door de trage diffusiesnelheid. Het breukvlak van het tijdens de trektest opgeladen duplex RVS vertoont quasi-splijting breuk in de zone getroffen door waterstof en ductiele breuk in het centrum van het breukvlak. Deze ductiele breuk wordt ook geobserveerd bij de referentietesten zonder waterstof. De kritische waterstofconcentratie voor quasi-splijting breuk wordt bepaald door de grootte van de brosse zone te linken met het waterstofconcentratieprofiel. Verder wordt een verandering in actieve vervormingsmechanismes geobserveerd wanneer waterstof aanwezig is. Dit wordt bestudeerd via diffractie van teruggekaatste elektronen (EBSD) op intermediair gestopte trektest materialen. Waterstof zorgt zowel voor meer planaire slip als voor de vorming van ε- en α'-martensiet. Dit effect wordt gelinkt aan de daling van de stapelfoutenergie (SFE) door waterstof en het immobiliseren van randdislocaties. Verder wordt ook waterstofgeassisteerde scheurvorming bestudeerd. Door de hoge waterstofconcentraties die in dit werk gebruikt worden, vindt scheurinitiatie vooral plaats

in het austeniet. De martensitische fasen zijn niet gevoelig voor scheurinitiatie. Scheurpropagatie gebeurt doorheen korrels van zowel austeniet als ferriet. Ten slotte kan ook geconcludeerd worden dat wanneer een hogere ferrietfractie aanwezig is door hittebehandeling, de waterstofverbrossing gevoeligheid toeneemt door de verhoogde gemiddelde waterstofdiffusiesnelheid.

Hoofdstuk 6 en 7 worden gewijd aan de eerste volledig austenitische staalsoort dat onderzocht werd, namelijk 304L RVS. Dit staal is metastabiel op kamertemperatuur wat betekent dat het transformeert naar a'-martensiet door vervorming. In hoofdstuk 6 wordt de invloed van voorvervorming op de waterstof oplosbaarheid en diffusiviteit onderzocht. Zowel elektrochemisch als gasvormig opladen worden gecombineerd met TDS en het numeriek model dat werd ontwikkeld in hoofdstuk 4. De aanwezigheid van a'-martensiet verlaagt de waterstofoplosbaarheid en verhoogde de waterstofdiffusiesnelheid. Een alternatieve methode voor de bepaling van de effectieve waterstofdiffusiecoëfficiënt wordt eveneens voorgesteld: waterstof desorptie-experimenten op constante temperatuur. De nodige voorwaarde van een homogene waterstofconcentratie doorheen de dikte wordt vervuld door de gasvormige oplaadmethode die op hoge temperaturen kon gebeuren.

In hoofdstuk 7 wordt de invloed van de verplaatsingssnelheid op de waterstofverbrossingsgevoeligheid van 304L RVS geëvalueerd. Hoe lager de vervormingssnelheid, hoe meer waterstof in staat is om het roestvaste staal te verbrossen door de tijd die beschikbaar is voor diffusie. Door het metastabiel karakter van het austeniet in 304L RVS stijgt de effectieve waterstofdiffusiecoëfficiënt continu tijdens de trektest waardoor deze roestvaste staalsoort gevoeliger is aan waterstof dan stabiele austenitische stalen. De martensitische transformaties hebben echter een positieve invloed op de maximale treksterkte en de verlenging bij breuk. Zowel het verhinderen van het adiabatisch opwarmeffect als de aanwezigheid van waterstof doen de α'-martensiet transformatie versnellen. Bovendien wordt er ook ε-martensiet gevormd terwijl deze niet aanwezig is in de referentietesten zonder waterstof. Wanneer zowel het waterstof als het temperatuureffect spelen en de martensitische transformaties hierdoor gepromoot worden tijdens trektesten aan hoge vervormingssnelheden, wordt een hogere verlenging bij breuk waargenomen ten opzichte van de referentie. Deze observatie suggereert dat waterstof ook een versterkend interstitieel element kan zijn. Dit opent opportuniteiten voor de ontwikkeling van waterstof-resistente legeringen. Verder wordt er in dit hoofdstuk ook aangetoond dat de zone getroffen door waterstof op het breukvlak quasi-splijting karakteristieken vertoonde en toeneemt in grootte met afnemende vervormingssnelheid. Ten slotte verhoogt de waterstofgevoeligheid wanneer het staal voorvervormd is door de vorming van microstructurele defecten en de verhoogde waterstofdiffusiesnelheid.

De tweede volledig austenitisch staalsoort dat bestudeerd wordt, is tweeling-geïnduceerde plasticiteit staal. In tegenstelling tot 304L RVS wat martensitische transformaties vertoonde, is deze staalsoort gevoelig voor vervormingsgeïnduceerde tweelingvorming. Drie verschillende TWIP stalen worden onderzocht: Fe-18Mn-0.6C, Fe-18Mn-0.6C-1.5Al en Fe-24.5Mn-0.6C TWIP staal. In de literatuur werd reeds vermeld dat toevoeging van aluminium een positief effect heeft op de weerstand tegen

waterstofverbrossing. Er wordt echter nog steeds gedebatteerd over het exacte mechanisme. Een mogelijk mechanisme is gelinkt met de verhoging van de stapelfoutenergie bij toevoeging van aluminium. Om het effect van de stapelfoutenergie verder te verhelderen wordt een TWIP staal gecreëerd met een gelijke stapelfoutenergie door de mangaanfractie te verhogen. De stapelfoutenergie wordt hierbij bepaald aan de hand van een thermodynamisch oplossingsmodel voor hoog-mangaan stalen. In hoofdstuk 8 worden de verschillen in oplosbaarheid en diffusie tussen de drie stalen opgehelderd. Toevoeging van aluminium verhoogt de oplosbaarheid en verlaagt in beperkte mate de diffusiesnelheid. Toevoeging van mangaan verhoogt ook de oplosbaarheid. De diffusiesnelheid wordt echter ook verhoogd bij een hogere mangaanfractie.

De invloed van waterstof op de mechanische eigenschappen van de drie TWIP stalen wordt onderzocht in hoofdstuk 9. Hoewel door toevoeging van aluminium de hoeveelheid waterstof in het staal toeneemt, kan er toch een gunstig effect waargenomen worden op de ductiliteit met waterstof na vergelijking van het relatieve verlies in verlenging bij breuk. Toevoeging van mangaan blijkt echter nefast voor de waterstofverbrossing gevoeligheid, ondanks de gelijkaardige SFE t.o.v. het TWIP staal waaraan aluminium werd toegevoegd. De reden voor dit verschil is tweevoudig. Enerzijds verlaagt aluminium de waterstofdiffusiesnelheid terwijl mangaan deze snelheid gevoelig verhoogt. Anderzijds verhoogt aluminium de bindingssterkte van de korrelgrenzen wat leidt tot een grotere weerstand tegen scheurinitiatie en een breukvlak dat hoofdzakelijk gekenmerkt werd door quasi-splijting. Mangaan verlaagt echter de bindingssterkte van de korrelgrenzen waardoor scheurinitiatie overvloedig voorkomt en het breukvlak vooral kristallijne breuk vertoont. Door het verschil in dominant breukmechanisme is de kritische waterstofhoeveelheid hoogst waarschijnlijk verschillend waarbij aluminium toevoeging duidelijk voordelig is. De waterstofgeïnduceerde daling van de SFE wordt opnieuw bevestigd voor de drie legeringen. Zowel het TWIP staal met aluminium als het Fe-24.5Mn-0.6C TWIP staal vertonen een hogere fractie aan tweelingen terwijl ε-martensiet gevormd wordt in het Fe-18Mn-0.6C TWIP staal wanneer waterstof aanwezig was.

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## Publications

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- L. Claeys, I. De Graeve, T. Depover and K. Verbeken, "Impact of hydrogen and crosshead displacement rate on the martensitic transformations and mechanical properties of 304L stainless steel", Theoretical and Applied Fracture Mechanics 113 (2021), 102952, <u>10.1016/j.tafmec.2021.102952</u>
- L. Claeys, I. De Graeve, T. Depover and K. Verbeken, "Hydrogen-assisted cracking in 2205 duplex stainless steel: initiation, propagation and interaction with deformation-induced martensite", Materials Science and Engineering A 797 (2020), 140079, <u>10.1016/j.msea.2020.140079</u>
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## Co-authored publications

- L. Rabelo Fernandes, L. Claeys, M. Pinson, T. Depover, D. Brandão Santos and K. Verbeken, "Evaluating the hydrogen embrittlement susceptibility of aged 2205 duplex stainless steel containing brittle sigma phase », Steel Research International (2021), accepted
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### Conference proceedings

• L. Claeys, A. Coone, T. Depover, I. De Graeve and K. Verbeken, "The effect of strain rate on the interaction between hydrogen and deformation-induced martensite in 304 austenitic stainless steel" (2019), Eurocorr conference proceedings

## Oral presentations

- Eurocorr Sevilla: L. Claeys, A. Coone, T. Depover, I. De Graeve and K. Verbeken, "The effect of strain rate on the interaction between hydrogen and deformation-induced martensite in 304 austenitic stainless steel" (2019)
- Eurocorr Krakau: L. Claeys, T. Depover, I. De Graeve and K. Verbeken, "Electrochemical hydrogen charging of duplex stainless steel" (2018)

## Poster presentations

- 2<sup>nd</sup> Benelux Network meeting and workshop on damage and fracture mechanics Antwerp L. Claeys, G.G. Braga, T. Depover, D. Brandão Santos and K. Verbeken, "The effect of hydrogen on the properties of duplex stainless steel" (2019) - Awarded best poster presentation
- SteelyHydrogen Ghent: L. Claeys, G.G. Braga, T. Depover, D. Brandão Santos and K. Verbeken, "The effect of hydrogen on the properties of duplex stainless steel" (2018)
- The challenges of hydrogen and metals London: A. Laureys, L. Claeys, T. De Seranno, T. Depover, R. Petrov and K. Verbeken, "Characterisation of hydrogen induced cracking in generic Fe-C-Ti and Fe-C-V alloys" (2017)

## List of symbols and abbreviations

a'- mart	Alpha prime martensite
ε- mart	Epsilon martensite
ΔG	Gibbs free energy [J/mol]
ΔΩ	Interaction energy [J/mol]
a	Cubic lattice parameter
AHSS	Advanced high strength steels
AIDE	Adsorption-induced dislocation emission
AISI	American iron and steel institute
ASS	Austenitic stainless steel
BCC	Body centered cubic
BCT	Body centered tetragonal
CI	Confidence index
Cs	Equilibrium surface hydrogen concentration
D <sub>eff</sub>	Effective hydrogen diffusion coefficient [m²/s]
Do	$eq:pre-exponential factor of the hydrogen diffusion coefficient \ [m^2/s]$
Dev	Deviation from the mean value
DSS	Duplex stainless steel
EBSD	Electron backscatter diffraction
EDX	Energy dispersive X-ray spectroscopy
FCC	Face centered cubic
FEG	Field emission gun
FIB	Focussed ion beam
Н	Hydrogen
HAC	Hydrogen assisted cracking
HAGB	High angle grain boundary
НСР	Hexagonal closed packed
HE	Hydrogen embrittlement
HEDE	Hydrogen-enhanced decohesion
HEDT	Hydrogen-enhanced densified twinning

HELP	Hydrogen-enhanced localised plasticity
HESIV	Hydrogen-enhanced strain-induced vacancies
НІРТ	Hydrogen-induced phase transformation
HV	Vickers hardness
IPF	Inverse pole figure
IQ	Image quality
LAGB	Low angle grain boundary
M <sub>d</sub>	Deformation-induced martensite start temperature [°C]
M <sub>s</sub>	Martensite start temperature [°C]
Ν	Avogadro's number (6.022E23 mol <sup>-1</sup> )
ND	Normal direction
OIM	Orientation imaging microscopy
Q	Diffusion activation energy [kJ/mol]
R	Gas constant (8.314 J mol <sup>-1</sup> K <sup>-1</sup> )
RD	Rolling direction
SE	Secondary electron
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
SF	Stacking fault
SFE	Stacking fault energy
stdev	Standard deviation
TD	Transverse direction
TDS	Thermal desorption spectroscopy
TEM	Transmission electron microscopy
TRIP	Transformation-induced plasticity
TWIP	Twinning-induced plasticity
UNS	Unified numbering system
UTS	Ultimate tensile strength
Wppm	Weight parts per million
XRD	X-ray diffraction
YS	Yield strength

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### Chapter 1 Introduction

#### 1.1. <u>Problem statement</u>

Hydrogen has drawn a lot of attention over the past decades and continues to gain a lot of interest. The present interest is mainly driven by the desire to create a hydrogen economy as hydrogen is a very efficient energy carrier. Hydrogen gas is regenerative requiring energy to be produced since it never appears in its pure form. Its combustion is free of CO<sub>2</sub>-emissions which is a major advantage given the current environmental concerns on global warming [1]. The European Green Deal of Nov. 19<sup>th</sup> 2019, clearly has put forward 'clean hydrogen' as one of the key technologies in the aim for climate-neutrality by 2050 [2]. The term clean refers to the energy needed for the production of hydrogen gas which should become green, i.e. a fully decarbonised hydrogen production. Many countries have already undertaken efforts towards a hydrogen-based energy supply which is capable of answering the needs of modern society, e.g. Norway, the Netherlands, the UK and Japan. The Olympic Village area in Tokyo was for example designed with a hydrogen station, a hydrogen pipeline and hydrogen fuel cells for transport, electricity and heat production [3]. Since Europe is recently emphasizing strongly on the large potential of hydrogen, many other European countries are preparing a transition as well, including Belgium.

Automotive industry has, also in the light of the strict regulations on the allowed CO<sub>2</sub>-emission level, focussed on reducing car weight while maintaining passenger safety in case of a crash and answering customer expectations regarding increased passenger comfort. This required the development of stronger steels that were still easily formable to the desired shape. Designing strong and at the same time ductile materials has, however, been one of the key challenges for metallurgists. The second generation advanced high strength steels were able to overcome this problem. This class of advanced high strength steels is austenite-based at room temperature, having a face centered cubic (FCC) crystal structure, and shows a high level of ductility combined with a high strength level due to the activation of alternative deformation mechanisms [4]. It includes austenitic stainless steels, twinning-induced plasticity (TWIP) steels and lightweight-induced plasticity (L-IP) steels, as indicated in Figure 1-1. Third generation advanced high strength steels are being developed to close the gap between the first and second generation [5].

Unfortunately, hydrogen presence inside metals can significantly deteriorate the mechanical properties. Being the smallest element in the periodic table, hydrogen resides in the interstitial positions of the metal's crystal lattice and is in many metals mobile at room temperature jumping from one interstitial position to the other. The first to report the negative consequences of hydrogen in a metal was Johnson [6] in 1875. The subject has gained a lot of attention since and is generally referred to as hydrogen embrittlement (HE) [7]. HE problems are immensely complex. It requires understanding of processes at the atomic level that impact the behaviour on the macroscopic scale [8]. In this regard, the development of hydrogen-resistant steels has become a bottleneck for the creation of gaseous hydrogen storage and transport infrastructures as well as hydrogen fuel cell and hydrogen engine materials for the hydrogen

#### Introduction

economy. Moreover, in automotive industry, hydrogen-induced delayed fracture is posing pertinent problems to the application potential of high strength steels. The main research efforts in terms of the second generation advanced high strength steels for automotive industry focus on twinning-induced plasticity steels [9]. Furthermore, in the oil and gas industry, stainless steels are increasingly used. Austenitic stainless steels are used for valves, pipes, heat exchangers, reactor claddings, ... [10] Many of the processes in oil and gas industry involve the presence of highly-corrosive environments inducing the possibility of creating hydrogen during the corrosion process. Stainless steels are ideal candidates for subsea applications related to oil and gas industry as well. Recent subsea failures were, however, ascribed to hydrogen-induced stress cracking. In the highly corrosive subsea environment, cathodic protection is typically applied to the stainless steel structures, which is a major source for hydrogen production. The increased hydrogen level in combination with high residual stresses in the material result in the mentioned hydrogen-related failures [11].

Austenitic steels were always regarded as very desirable materials when it comes to HE. This is mainly related to their FCC crystal structure, which, due to its close packing, is characterised by a very low hydrogen diffusivity at room temperature. In body centered cubic (BCC) steels, the diffusivity at room temperature is typically five to six orders of magnitude higher [12]. Despite their intrinsically preferable diffusion properties, austenitic steels suffer from HE and related phenomena as well, e.g. delayed cracking of TWIP steels and failure of subsea components as mentioned in the previous paragraph. Compared to the first generation advanced high strength steels, most research efforts on the hydrogen interaction with austenitic steels are much more recent. The large application potential of the austenitic steel types including automotive and hydrogen engine parts, transportation and storage infrastructures, subsea and other harsh environment applications, justifies further research efforts to improve the HE resistance and to better understand the HE phenomenon in FCC steels in general.





#### 1.2. <u>Objectives</u>

The main research objective of this PhD comprises of a profound characterisation of the interaction between hydrogen and the microstructure of FCC-containing steels in order to increase the current-state knowledge on this subject. Building upon the gained expertise in the research group at Ghent University on the interaction between hydrogen and the microstructure of BCC steels, advanced material characterisation techniques (e.g. electron backscatter diffraction) will be combined with high-level hydrogen characterisation techniques (e.g. thermal desorption spectroscopy) in this PhD as well.

The goal of the PhD comprises both of gaining more understanding on the phenomena happening during hydrogen charging and on the evaluation of the effect of hydrogen on the mechanical performance. Figure 1-2 schematically illustrates the subdivision of the PhD into two sub-objectives (part A and B), which will, once combined, give rise to a better understanding of the hydrogen interaction with austenite-containing steels. In the first sub-objective, hydrogen absorption, diffusion and trapping will be evaluated. In the second sub-objective, mechanical properties will be evaluated with and without hydrogen. Moreover, a lot of controversy exists on the interaction between hydrogen and the alternative deformation mechanisms of FCC steels. Characterisation of the influence of hydrogen on the active deformation mechanism is, therefore, an important goal of the second sub-objective. The influence of certain deformation-induced features on the sensitivity to cracking will be investigated as well. The obtained knowledge will be combined and discussed in terms of strategies to improve the HE sensitivity of FCC steels.



Hydrogen interaction with austenitic steels

Figure 1-2: Schematic illustration of the objectives of the PhD

#### Introduction

#### 1.3. <u>Outline</u>

Figure 1-3 schematically illustrates how the PhD chapters were defined. First, two introductory chapters will be presented. **Chapter 2** gives an overview of the most relevant literature on the subject of this PhD including a discussion on the relevant concepts about deformation of austenite and hydrogen embrittlement with main focus on austenitic steels. **Chapter 3** is dedicated to the experimental methodologies that were designed as well as to a general description of the used experimental techniques throughout the PhD.

The chapters following these introductory chapters were ordered with respect to the studied material. For every material type, two major parts were addressed based on the defined sub-objectives in Figure 1-2. The first part focussed on the hydrogen charging procedure including microstructural analysis, the amount of hydrogen charged into the steels and the evaluation of thermal desorption spectroscopy data (A in Figure 1-3). The second part focussed on the effect of hydrogen on the mechanical properties and the active deformation mechanisms (B in Figure 1-3).

The aim of this work was to investigate the hydrogen interaction with austenitic steels. Before focussing on fully austenitic steels, the first research step was the study of the hydrogen interaction with duplex stainless steel. This two phase steel type typically consists of 50% austenite combined with 50% ferrite. The work on duplex stainless steel can thus be seen as an intermediate step towards the study of fully austenitic steels. The evaluation of the hydrogen charging procedure and thermal desorption spectroscopy data (part A) on this material type can be found in **Chapter 4**. In this chapter, both experimental and numerical work is presented. The numerical part forms a basis for the part A chapters of the other, fully austenitic steels. In **Chapter 5**, hydrogen-induced mechanical degradation (part B) of duplex stainless steel is evaluated with major focus on the applied hydrogen precharging time and the initiation and propagation of hydrogen-assisted cracks.

The first fully austenitic steel studied in this PhD, is 304L austenitic stainless steel. The austenite matrix is metastable upon deformation and tends to transform to martensite. The influence of these martensitic transformations on the hydrogen-related properties was the major focus throughout the research on this steel type. In **Chapter 6**, the charging procedure and thermal desorption spectroscopy data (part A) are discussed for as-received and predeformed specimens. The hydrogen-induced mechanical degradation (part B) is elaborated in **Chapter 7**. In addition to the effect of the deformation-induced martensitic transformation, the effect of the strain rate on the degree of embrittlement is discussed as well.

The second fully austenitic steel type that was studied, is high manganese twinning-induced plasticity steel. Upon deformation, this steel type undergoes twinning which has a distinct influence on the hydrogen properties as well. The main focus of the two chapters dedicated to TWIP steels was to elucidate the effect of aluminium addition since this was stated to improve the hydrogen embrittlement resistance of TWIP steels. **Chapter 8** is again a part A chapter in which special attention is paid to homogeneously charge a

TWIP steel through electrochemical methods. The mechanical data is discussed in **Chapter 9** (part B) where the stacking fault energy of the TWIP steel plays a central role in the research strategy.

In **Chapter 10**, general conclusions for the different studied materials are given and suggestions for further research are put forward.



### Figure 1-3: Schematic illustration of the outline of the PhD including the different chapters

Introduction

## Chapter 2 State-of-the-art

### 2.1. Introduction

Iron is polymorphic, i.e. it can appear in different crystal structures. The crystal structure has an effect on the properties of iron alloys. Morever, these alloys often consist of a combination of crystallographic phases and microstructural constituents. The phases relevant for this PhD and their crystal structures are listed below:

- Ferrite, a: body centered cubic (BCC)
- Austenite, y: face centered cubic (FCC)
- ε-martensite: hexagonal close packed (HCP)
- a'-martensite: body centered tetragonal (BCT)

A schematic representation of the unit cell of the BCC, FCC and HCP crystal structures can be found in Figure 2-1. The black dots indicate where the iron atoms are located. The BCT crystal structure has a similar atom arrangement as the BCC crystal structure. However, one of the lattice parameters has a different size compared to the other two parameters while the BCC crystal structure has three equal lattice parameters (cubic).



Body-centered cubic



Face-centered cubic



Hexagonal close packed

# Figure 2-1: Schematic representation of the arrangement of the atoms for different crystal structures relevant for iron alloys [13]

The FCC and HCP crystal structures are close-packed. They can be built by stacking of closed-packed planes in a certain sequence. An ABABABAB stacking sequence results in an HCP lattice while the FCC structure is characterised by an ABCABCABC stacking [14]. Both stacking sequences are illustrated in Figure 2-2. The

#### Literature overview

BCC and BCT crystal structures are not close-packed. In iron alloys, a'-martensite has limited tetragonality and is often referred to as a BCC structure.



Figure 2-2: Formation of the HCP and FCC crystal structure by the stacking of closed-packed planes

In this PhD, austenitic steels exhibiting an FCC crystal structure are studied. This chapter will therefore focus on this steel type. The chapter is subdivided in two major parts. The first part provides a theoretical background of the deformation mechanisms that are characteristic for austenitic FCC steel types. In the second part, the available literature on hydrogen embrittlement is summarised. A general discussion on the phenomenon is given followed by a more in depth literature overview on hydrogen embrittlement and related phenomena in austenitic steels. Literature surveys on the specific materials and the used techniques in this PhD can be found in the following chapters.

#### 2.2. <u>Deformation mechanisms in austenite</u>

FCC metals can be subjected to different deformation and strengthening mechanisms. These mechanisms include dislocation glide, dissociation of dislocations into partial dislocations with the associated formation of a stacking fault, mechanical twinning and mechanical-induced phase transformation. Several austenitic steels exhibit a twinning-induced plasticity (TWIP) or a transformation-induced plasticity (TRIP) effect as a result of the mechanical twinning or mechanical-induced phase transformations, respectively [14]. Figure 2-3 shows two schematic flow curves (stress versus elongation). The lower curve describes the basic behaviour of FCC steel with solely dislocation glide and no alternative deformation mechanisms. In the upper curve, a TRIP/TWIP effect was added resulting in a simultaneous increase of the ultimate tensile strength ( $\Delta\sigma$ ) and uniform elongation ( $\Delta\epsilon$ ) of the material [15].

The mentioned concepts will be explained in more detail in the following sections. First, the concept of a stacking fault and its relation to the operative deformation mechanism is explained. Thereafter, mechanical twinning and mechanical-induced phase transformations are considered for austenitic steels. Hence, the latter will focus on the different types of the austenite to martensite transformation.

#### Chapter 2



Figure 2-3: Schematic flow curves with and without TRIP/TWIP effect [15]

### 2.1.1. Stacking faults

A stacking fault is a defect in a metal lattice defined by a fault in the succession of the different lattice planes. The energy difference that can be associated with the presence of this lattice defect is called the stacking fault energy (SFE). Two different types of stacking faults exist in FCC steels: intrinsic and extrinsic stacking faults. When the stacking fault character is intrinsic, it can be interpreted as a plane in the stacking sequence has been suppressed. On the contrary, in the case of an extrinsic stacking fault, a crystallographic plane has been added to the stacking sequence. Figure 2-4 schematically illustrates how the stacking fault is created in both cases (please note this is not what physically happens).

Intrinsic stacking fault	<u>Extrinsic</u> stacking fault
➡ АВСАВСА́ВСАВС ➡ АВСАВСВСАВСА	А В С А В С А В С А В С А В С А В С В А В С А В
Plane A has been suppressed	Plane B has been added

### Figure 2-4: Schematic representation of an intrinsic and extrinsic stacking fault in FCC metals

As two different stacking fault types exist, two different stacking fault energies can be defined as well. In general, the intrinsic stacking fault energy is lower than the extrinsic one and different materials are typically compared based on their intrinsic SFE value. There are different possibilities to determine the SFE experimentally, e.g. through X-ray diffraction (XRD) or transmission electron microscopy (TEM). Several parameters were found to influence the SFE of a material, e.g. its chemical composition and the temperature [16]. A discussion on these parameters is given hereafter.

#### Literature overview

Schramm and Reed [17] proposed a linear relation for the dependence of the SFE on the chemical composition of austenitic stainless steels. The authors used XRD measurements to obtain the SFEs of seven different austenitic stainless steels. The approach to determine the SFE makes use of the root-mean-square micorstrain in the {111} plane, the stacking fault probability and the lattice parameter determined by XRD after a Rietveld analysis of powder diffraction data [18]. The resulting expression for the chemical composition correlated well with the performed experiments:

SFE = 
$$-53 + 6.2(\%Ni) + 0.7(\%Cr) + 3.2(\%Mn) + 9.3(\%Mo) [mJ/m2]$$
 (2-1)

According to Rhodes and Thompson [19], large discrepancies exist, however, when evaluating stainless steels with other compositions. They concluded that the dependency is complex and generally nonlinear. For ternary alloys, the equations were subdivided between low Cr (<20 wt%) and high Cr (> 20 wt%) materials. For commercial alloys containing more than 18 wt% of Cr and a significant amount of manganese and silicon, the authors determined the following adapted equation:

Dumay et al. [20] calculated the influence of several alloying elements on the SFE of high-manganese TWIP steel. Figure 2-5 summarises the results. Al and Cu increased the SFE with Al having the largest effect while Cr reduced the SFE. Si had a more complex influence as a function of its content. Saeed-Akbari et al. constructed composition-dependent SFE maps for high-manganese steels based on a thermodynamic subregular solution model for high-manganese steels (10 < wt%Mn < 35 and 0 < wt%C < 1.2) showing a complex nonlinear behaviour for this steel class as well [21].



Figure 2-5: Predicted influence of alloying elements on SFE in Fe-22Mn-0.6C TWIP steel [20]

It is relatively well known that the stacking fault energy increases with increasing temperature. Remy [22] measured for example the intrinsic SFE of a high manganese steel in the temperature range 100-390K

with TEM and concluded that the SFE increased with temperature. As TEM is able to visualise stacking faults, the stacking fault width can be determined which is inversely proportional to the SFE, as discussed further on in this section. In a review by Remy et al. [23], it was also stated that in virtually all FCC materials, the SFE increased with temperature.

In general, plastic deformation corresponds to the motion of a large number of dislocations through the crystal lattice [14]. During this motion, atoms move from their position to the next similar position with one Burgers vector along the slip direction and on the slip plane of a certain crystal structure. For an FCC crystal structure, the slip systems comprise of {111}<110> which yields in total 12 different possibilities. When a moving dislocation encounters an obstacle, dislocations can cross-slip from one slip plane to another and continue their motion. Dislocations can, however, also separate into two partial dislocations and as such reduce their energy. When the first (or leading) partial dislocation moves through the lattice, the atoms are moved to an intermediate position corresponding to another stacking sequence, cf. Figure 2-2, i.e. an intrinsic stacking fault is created. When the second (or trailing) partial dislocation passes, the atom moves back to its original stacking sequence and the stacking fault is annihilated. Different possibilities exist for the splitting of dislocations. First, a dislocation can dissociate into two glissile Shockley partials. An example of such a reaction is [24]:

$$\frac{a}{2}[\bar{1}10] \to \frac{a}{6}[\bar{1}2\bar{1}] + \frac{a}{6}[\bar{2}21]$$
(2-3)

Secondly, the dissociation can occur as a glissile Shockley and a sessile Frank partial dislocation. In the latter case, the FCC stacking will not be restored when the first Shockley partial dislocation has passed as the Frank partial dislocation is sessile, i.e. locked. An example of this reaction is [24]:

$$\frac{a}{2}[01\bar{1}] \to \frac{a}{6}[21\bar{1}] + \frac{a}{3}[\bar{1}1\bar{1}]$$
(2-4)

When a Shockley partial dislocation is accompanied by another Shockley partial dislocation on the next close-packed plane, an extrinsic stacking fault is formed. This type of stacking fault can thus be regarded as a double stacking fault [24].

A stacking fault is characterised by an equilibrium width as a result of the repulsive forces between the partial dislocations driving them further apart and the creation of an increasingly larger stacking fault with its associated stacking fault energy. The equilibrium width is thus determined by the SFE and is in fact, inversely proportional to it. High SFE materials, therefore, disfavour the separation of dislocations into partials. When the SFE is low, however, dislocation splitting is very likely to occur. The movement of Shockley partial dislocations is always restricted to the glide plane preventing them from cross-slipping to another slip plane and as such triggering other deformation mechanisms [25]. The SFE is therefore the most important parameter influencing the operative deformation mechanism. For austenitic steels, the following order applies with decreasing SFE: dislocation glide and cross-slip, mechanical twinning,

#### Literature overview

martensitic transformation. Several authors determined ranges for the intrinsic stacking fault energy where the different deformation mechanisms are active as illustrated in Figure 2-6 [26, 27, 28].



Figure 2-6: Schematic illustration of the dependence of the operative deformation mechanism on the intrinsic SFE for Fe-Mn-C [27], Fe-Mn-Cr-C [26] and Fe-18Cr-10Mn-N-C [28]

#### 2.1.2. Mechanical twinning

Mechanical twinning is an important deformation mechanism in FCC metals and alloys and therefore deserves more in-depth attention. Twinning results in a product which has an identical crystal structure as the matrix but a different crystallographic orientation. In FCC materials, the twin orientation corresponds to a rotation of 180° around the twin plane normal, typically a {111} plane, which is equal to a 60° rotation around the [111] direction since this is a three-fold symmetry axis. The twin plane itself remains unchanged, i.e. twinning is characterised by an invariant plane strain. Since no volume change is involved, deformation twinning occurs more specifically by simple shear.

Deformation twinning can be understood as a homogeneous shear of the austenite matrix by a highly coordinated glide of partial dislocations along a <112> direction with the same burgers vector on a successive {111}-plane. The intrinsic stacking faults associated with the partial dislocations subsequently
overlap resulting in the formation of a twin embryo. Twin growth occurs by the addition of stacking faults to the twin embryo. Several mechanisms have been proposed involving the necessary dislocation activity. It is clear that the models require an explanation for the formation of partial dislocations on every close-packed plane and a process which suppresses the movement of the trailing dislocation [29]. The Venables pole mechanism suggests for example that a Shockley partial dislocation moves away from a Frank partial (the pole dislocation) and rotates around the pole dislocation winding down to the underlying plane [30].

Three models are put forward to explain the enhanced work hardening by deformation twinning. As deformation twins locally harden the areas where they are formed, other grains that have not yet undergone deformation twinning will deform first. This postpones plastic instability during deformation leading to an increase in uniform deformation before necking, i.e. the TWIP effect. In the first hardening mechanism, it is assumed that mechanical twins can act as planar obstacles to dislocation glide reducing the main free path A and enhancing dislocation storage [31]. This idea is schematically illustrated in Figure 2-7 (a). This effect is often referred to as the dynamic Hall-Petch effect due to the resemblance with the grain size (Hall-Petch) effect on flow stress. An equation was proposed to calculate the dynamic Hall-Petch effect:

$$\sigma = \sigma_0 + k \frac{G \cdot b}{t} n \tag{2-5}$$

Where  $\sigma_0$  is the flow stress of the untwinned matrix, k is a constant, G is the shear modulus, b is the magnitude of the burgers vector, n the number of dislocations in the pile-up and t the mean distance between adjacent twins. This distance t is a function of the twin volume fraction and the twin thickness which changes with increasing strain [32].

Secondly, Bouaziz et al. [33] stated that the back stress is generated by dislocation pile-ups arrested at mechanical twin boundaries. The back stress may be written in its simplest form as

$$\sigma_{BS} = M \frac{G \cdot b}{L} n \tag{2-6}$$

Where M is the average Taylor factor and L the geometrical length scale of the microstructure [34]. Since grain and twin boundaries can be considered as the main obstacles, L can be written as

$$\frac{1}{L} = \frac{1}{d} + \frac{1}{t} \tag{2-7}$$

Where d is de grain size (diameter). A schematic representation of the back stress effect is given in Figure 2-7 (b).

Finally, strain compatibility between the austenite matrix and the twin requires the generation of backward and forward internal stresses. The backward stresses develop in the soft austenite matrix while the forward stresses develop in the hard twins leading to a composite strain hardening effect, cf. Figure 2-7 (c) [35].



Figure 2-7: Schematic illustration of several mechanisms for plasticity enhancement due to deformation twinning: (a) the dynamic Hall-Petch effect., (b) the back stress effect, and (c) the composite strain hardening effect [36]

#### 2.1.3. Martensitic transformations

Martensitic transformations are diffusionless phase transformations. They can be subdivided in different categories: thermal martensite, stress-induced martensite and strain-induced martensite. Thermal martensite is formed by cooling below the martensite start temperature, M<sub>5</sub>. Stress-induced transformation implies the presence of nucleation sites that were formed during cooling and are triggered to form martensite under an applied stress below the yield stress. This leads to an increase of the strength while the plasticity decreases, i.e. no TRIP effect can occur as a result of these transformations [15]. Strain-induced martensitic transformation takes place during plastic deformation and is governed by the production of new nucleation sites [37]. Strain-induced martensite is responsible for the TRIP effect [15]. A martensite deformation temperature M<sub>d</sub> can be defined which represents the temperature above which no phase transformations occur by plastic deformation, i.e. a measure for the austenite stability. The concept of the M<sub>d30</sub> temperature was subsequently introduced, since the M<sub>d</sub> temperature was hard to measure, referring to the temperature at which 50% of martensite is formed at a tensile strain of 30%. For austenitic stainless steels, the following formula was determined based on the chemical composition of the alloy (within a certain validity range) [38]:

Martensite transformation is also characterised by an invariant plane strain meaning that one plane remains unchanged during the transformation. This plane is the habit plane of the transformation. Unlike twinning, the martensitic transformation is accompanied by a volume change. Two different types of martensite can form in FCC iron:  $\varepsilon$ -martensite with an HCP crystal structure and  $\alpha$ '-martensite with a BCT (nearly BCC) crystal structure. Three different transformation routes exist:  $\gamma \rightarrow \varepsilon$ ,  $\gamma \rightarrow \alpha$ ' and  $\gamma \rightarrow \varepsilon \rightarrow \alpha$ '. The martensite type occurring in a specific steel depends on the chemical composition of the material and the temperature since it is governed by the austenite stability and SFE. It is usually stated that the transformation to  $\alpha$ -martensite takes place for lower SFEs than the transformation to  $\epsilon$ -martensite [39]. However, the interaction with phase stability is not sufficiently taken into account. As a result, it is possible to have  $\alpha$ '-martensite formation when the SFE is even high enough to prevent  $\epsilon$ -martensite formation [40].

The formation of  $\varepsilon$ -martensite can, similarly as for deformation twinning, be explained by the activity of partial dislocations. Brooks et al. [41] concluded that an intrinsic stacking fault is on itself an embryo for  $\varepsilon$ -martensite since it contains a small HCP stacking sequence, cf. Figure 2-4. A low SFE thus favours  $\varepsilon$ -martensite formation since the stacking fault extends over a large distance. Stacking of extrinsic stacking faults on every {111} plane results in  $\varepsilon$ -martensite growth. From a crystallographic point of view, this is equivalent to the stacking of intrinsic stacking faults on every second {111} plane. As for twinning, mechanisms exist to explain the generation of the right dislocations. To attain a true  $\varepsilon$ -martensite structure, the interatomic spacing between the (0001) planes must change. However, this change is very small (0.1%) and it seems reasonable that the misfit is accommodated by the nucleation of dislocations.

The initiation of a'-martensite directly from austenite cannot be explained by a simple sequence of stacking faults. However, in-situ observations showed that the nucleation and growth of a'-martensite involved faulted regions in dislocation pile-ups. Due to the applied stress during deformation, dislocation partials are forced closer together. The atomic structure close to the core resembles the BCC stacking. The BCC crystal structure volume increases as more dislocations join the pile-up until the formed nucleus reached a critical size and rapid growth takes place [41]. Alternatively, a'-martensite can form at the intersections of slip bands. Olsen and Cohen developed a mechanism for this transformation which is illustrated in Figure 2-8 [42]. Intersections of  $\varepsilon$ -martensite laths can similarly serve as initiation sites for a'-martensite giving rise to the consecutive  $\gamma \rightarrow \varepsilon \rightarrow a'$  transformation [43].

The crystal structures of austenite and both types of martensite are crystallographically related through orientation relationships. The Kurdjumov-Sachs relationship [44] relates austenite to α'-martensite while the Shoji-Nishiyama [45] relationship relates ε-martensite to α'-martensite leading to the following relationships between the three phases:

$$\{111\}_{\gamma} // \{0001\}_{\epsilon} // \{110\}_{\sigma'}$$
 (2-9)

$$<110>_{\gamma} // < \overline{2}110>_{\epsilon} // <111>_{\sigma}$$
 (2-10)

Alternatively, the Nishiyama-Wasserman [46] orientation relationship between austenite and a'martensite was defined as follows:

$$\{111\}_{\gamma} // \{110\}_{\alpha'}$$
 (2-11)

The two alternative orientation relationships are schematically presented in Figure 2-9. Other orientation relationships have been presented as well but the Kurdjumov-Sachs and Nishiyama-Wasserman relationships are most successful in describing the correlation based on experiments [47].

Several explanations were put forward to explain the hardening effect by martensitic transformations leading to the TRIP effect. Similarly as for twinning, the formation of martensite creates new boundaries which limit dislocation mobility leading to work hardening. A composite effect was proposed as well since the formed martensite phase is usually harder than the austenite matrix resulting in work hardening of the surrounding matrix. Additionally, the Greenwood–Johnson effect corresponds to the plastic strain induced in the parent austenite phase due to the volume change provoked by the transformation [48]. The latter effect is mainly associated with the a'-martensitic transformation.

It should be noted that the TWIP and TRIP effects are not equally pronounced in every FCC material showing either deformation twinning or deformation-induced martensitic transformations. The effect is largely controlled by the formation kinetics. Too fast kinetics lead to premature failure since dislocation motion is hindered too soon. With too slow kinetics, there is insufficient twin/martensite formation to postpone necking also leading to premature failure.



Figure 2-8: Schematic illustration of intersecting shears, one array has Shockley partials on every third {111}<sub>y</sub> plane while the other array has Shockley partials on every second {111}<sub>y</sub> plane. The resulting double faulted intersection has a BCC structure [42]

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Figure 2-9: Schematic representation of the orientation relationships between austenite (FCC) and a'-martensite (BCC) (a) Kurdjumov-Sachs and (b) Nishiyama-Wasserman [47]

# 2.2. <u>Hydrogen embrittlement</u>

2.2.1. General introduction

Hydrogen embrittlement (HE) is a metal degradation phenomenon that occurs at ambient temperatures when a relatively small hydrogen concentration (ppm-level) is present in the material. It is a complex phenomenon manifested at different length scales. Metals suffering from HE show a reduced ductility, loss of their load-bearing capacity, the occurrence of cracking, a reduction in fracture toughness and sometimes even catastrophic failure at stresses far below what could be expected. Hydrogen has been reported to alter the fracture mechanism of a metal. Ductile fracture by microvoid coalescence can change to brittle intergranular fracture, cleavage or quasi-cleavage (combining the characteristics of cleavage fracture with ductile dimples) fracture [49, 50].

Three different types of cracking can be defined: hydrogen-assisted cracking (HAC), hydrogen-induced cracking (HIC) and delayed cracking. HAC occurs when an external stress is applied and cracks appear due to the presence of both hydrogen and applied stress. At highly stressed regions such as crack tips or notches, hydrogen accumulation takes place. As a consequence, cracking occurs at lower stress levels [51]. HIC is caused by the exposure of a material to a hydrogen-rich environment in the absence of an applied stress. Cracks form by an internal pressure build-up caused by hydrogen recombination to H<sub>2</sub> [52]. If the cracks form just below the surface, the external layer of the metal can become lifted, creating hydrogen blisters [52]. Delayed cracking occurs in materials containing hydrogen that suffer from high residual stresses, e.g. from the production process. Delayed cracking appeared in deep-drawn TWIP parts after exposure to air or submersion in water. It typically starts at the cup edge and subsequently propagates along the cup forming direction as can be seen in Figure 2-10 (a) [53] . The crack appearance could be directly related to the presence of residual tensile stresses in the cup as calculated through FE simulations on Fe-22Mn-0.6C TWIP steel and presented in Figure 2-10 (b) [54].



Figure 2-10: Delayed cracking of Fe-22Mn-0.6C TWIP steel [53] (a), distribution of simulated residual stress components after cup forming (b) [54]

Hydrogen can enter a metal by adsorption at the surface and subsequent absorption from its surrounding atmosphere. This atmosphere can either be a gaseous phase or an electrolyte. In a gaseous environment, the hydrogen molecules undergo physisorption on the surface followed by either direct dissociation to hydrogen atoms (chemisorption) or surface diffusion and then dissociation. In an electrolyte, electrochemical reduction reactions take place (or can be provoked). Depending on the nature of the environment, the adsorption can be seen as follows [12]:

$$H_2(g) \leftrightarrow H_{ads} + H_{ads}$$
 (gaseous environment) (2-13)

$$H^* + e^- \leftrightarrow H_{ads}$$
 (acid environment) (2-14)

$$H_2O + e^- \leftrightarrow H_{ads} + OH^-$$
 (alkaline environment) (2-15)

As hydrogen has a small atomic radius (the smallest element in the periodic table), it resides in the interstitial voids of a crystal structure when it is absorbed. Two types of interstitial lattice sites exist in the most important iron crystal structures, i.e. a tetrahedral interstitial lattice site having a coordination number of 4 and an octahedral site with a coordination number of 6 [14]. The preferential interstitial site for hydrogen to reside in BCC iron is the tetrahedral site since this void has the largest size. On the contrary, the preferential interstitial site in FCC and HCP iron is the octahedral site [55].

The lattice solubility of hydrogen in metals depends on the crystal structure, chemical composition and temperature. The lattice solubility of austenitic steels is up to three orders of magnitude higher than that of BCC iron as the preferred octahedral site for FCC iron is larger than the preferred tetrahedral site for BCC iron. The presence of substitutional atoms in a crystal structure influences the interstitial void size, hence, altering the hydrogen solubility. The solubility also increases with increasing temperature due to an increase in void size (thermal expansion). The hydrogen solubility/temperature dependency for different FCC steels is shown in Figure 2-11. Data for the lattice solubility of BCC iron (a-Fe) are added as well [12].



Figure 2-11: H solubility/temperature dependency for stainless steel [12] (data from [56])

Within a metal lattice, hydrogen diffusion takes place, i.e. hydrogen 'jumps' from one interstitial position to the neighbouring interstitial position driven by a gradient in concentration or stress. Hirata et al. [55] performed a first principles study on the diffusivity of hydrogen in BCC, FCC and HCP iron. Figure 2-12 shows the results of the study where hydrogen atoms are visualised on different migration paths in the three iron lattices. O represents an octahedral position, T a tetrahedral position and S a saddle point crossed on the migration path from one interstitial position to another. The associated migration energy for the different migration paths is given as well. The hydrogen diffusivity can be estimated based on this migration energy  $\Delta E$  with the following formula:

$$D = nL^2 \frac{k_B T}{h} exp(-\frac{\Delta E + \Delta G_{vib}}{k_B T})$$
(2-16)

Where D is the diffusion coefficient  $[m^2/s]$ , n a numerical coefficient, L the jump distance,  $k_B$  the Boltzmann constant, T the temperature, h the Planck constant,  $\Delta E$  the migration energy and  $\Delta G_{vib}$  the vibrational free energy. Hydrogen diffusivity was highest in the BCC lattice exceeding the value of FCC iron with about five orders of magnitude. The diffusion coefficient in the FCC lattice was found to be slightly higher than for the HCP lattice. In the latter case, hydrogen diffusivity depended on the c/a axis ratio as illustrated in Figure 2-13. It is clear that the hydrogen diffusion coefficient D  $[m^2/s]$  has a strong dependency on the temperature as well. It increases with increasing temperature through an Arrhenius relationship typically expressed as:

$$D = D_0 \exp(-Q/RT)$$
 (2-17)

with  $D_0$  a pre-exponential factor [m<sup>2</sup>/s], Q the diffusion activation energy [J/mol], R the universal gas constant [J/K/mol] and T the temperature [K].

The reason for the higher hydrogen diffusivity of the BCC lattice compared to the FCC and HCP lattice can be regarded as twofold. First, the BCC structure is not a close-packed structure meaning that hydrogen can move easier in the space between the iron atoms. Secondly, more tetrahedral interstitial positions are available in the BCC lattice compared to the number of octahedral interstitial positions in the FCC and HCP lattices [14].



Figure 2-12: First-principles study of hydrogen diffusivity in BCC, HCP (c/a = 1.58) and FCC iron, (a) representation of the diffusion paths, (b) energy profile for the presented paths of BCC and HCP, for FCC the energy profiles are subdivided to distinguish between the nonmagnetic (b), antiferromagnetic FCC (c) and antiferromagnetic FCT (d) condition [55]



Figure 2-13: Diffusion coefficient as a function of the inverse temperature for antiferromagnetic FCC and HCP with different c/a ratios based on first principle calculations [55]

During its migration through the metal lattice, hydrogen interacts with different microstructural defects. Hydrogen can be trapped at these defects, i.e. maintained longer than in normal interstitial lattice sites. Figure 2-14 shows typical hydrogen trapping sites in the microstructure including free surfaces and sites between the first atomic layers, dislocations, grain boundaries, vacancies and vacancy clusters, interfaces of precipitates and inclusions, phase boundaries, internal crack tips, etc. [57]. Figure 2-15 schematically

illustrates hydrogen trapping from an energetic point of view [58]. During diffusion between interstitial lattice sites I<sub>s</sub>, hydrogen atoms overcome a barrier with energy Q, i.e. the diffusion activation energy, for every consecutive jump. When a hydrogen trapping site T<sub>s</sub> is encountered, the hydrogen atom needs to overcome the saddle point energy E<sub>s</sub> after which the total energy of the system is lowered. When hydrogen leaves a trapping site, it needs to overcome the trap desorption activation energy E<sub>D</sub> which can be interpreted as the sum of the saddle point energy and the trap binding energy E<sub>B</sub>. Figure 2-15 gives a possible interpretation of the different energies, however, several variants are possible as well. The saddle point energy barrier might even be very large making it nearly impossible for hydrogen to enter the trap site at ambient conditions.

A distinction was made between hydrogen trapping sites based on their binding energy. Reversible (weak) trapping sites have binding energies below 30 kJ/mol while irreversible (strong) trapping sites are characterised by a binding energy above 60 kJ/mol [59]. The threshold values are a rather arbitrary choice and have no further physical meaning [60].

In literature, values for the binding and desorption activation energy of hydrogen trapping sites are abundantly present. Some examples for the binding energy with increasing trap strength are: dislocations 20-26 kJ/mol, grain boundaries 26-59 kJ/mol, vacancies and vacancy clusters 40-70 kJ/mol and the interface of TiC precipitates 77-96 kJ/mol [61, 62, 60, 63].



Figure 2-14: Schematic representation of different possible trapping sites in a metal microstructure [57]

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Figure 2-15: Energy levels of hydrogen with trapping; Q = diffusion activation energy; E<sub>s</sub> = saddle point energy; E<sub>B</sub> = trap binding energy; E<sub>D</sub> = trap desorption activation energy; T<sub>s</sub> = trapping site, I<sub>s</sub> = normal lattice site (adapted from [58])

Experimental studies have pointed out that HE is mainly caused by diffusible hydrogen atoms, i.e. hydrogen atoms that are able to readily diffuse to sensitive locations in the microstructure. Researchers have therefore tried to make use of the presence of hydrogen trapping sites in a metal microstructure to limit hydrogen migration through the lattice. The traps should, however, be carefully designed since both reversible and irreversible trapping sites can negatively influence the HE resistance. Reversible trapping sites in the vicinity of a growing crack are considered beneficial since they extract hydrogen from interstitial lattice sites (hydrogen sink). The reversible character, however, also implies that such a hydrogen near crack tips (hydrogen source). Irreversible trapping sites, e.g. MnS inclusions or carbides, reduce the amount of hydrogen that can readily diffuse and are therefore assumed to be beneficial. In general, hydrogen will not be released from irreversible trapping sites [59]. However, crack initiation might take place at irreversible trapping sites due to the accumulation of hydrogen [64, 65, 66, 67].

Due to the presence of hydrogen traps linked to microstructural defects, the effective hydrogen diffusivity is lower than the predicted lattice hydrogen diffusivity as calculated and presented in Figure 2-12. The effective diffusivity is determined in experimental research and includes the influence of hydrogen trapping sites. It not only depends on the trap energy but also on the trap density. As a comparison, the effective hydrogen diffusion coefficient for different steel types is given in Table 2-1 including the experimental technique that was used for the determination. From the values in the table, it is clear that the hydrogen diffusivity in FCC steels is five to six orders of magnitude lower than the hydrogen diffusivity in BCC iron.

Steel type	H diffusion coefficient (m²/s)	Type of experiment	Source
Armco iron	5.9 x 10 <sup>-10</sup>	Electrochemical permeation	[68]
Dual phase steel (46.7% martensite)	2.9 x 10 <sup>-11</sup>	Electrochemical permeation	[69]
TRIP steel (13.2% austenite)	1.0 x 10 <sup>-11</sup>	Electrochemical permeation	[70]
Ferritic stainless steel AL 29-4-2	1.1 x 10 <sup>-11</sup>	Extrapolation of gas phase permeation data	[71]
Duplex stainless steel UNS S32205	6.4 x 10 <sup>-14</sup>	Electrochemical permeation	[72]
TWIP steel Fe-18Mn-0.6C	7.11 x10 <sup>-15</sup>	Extrapolation of gas phase permeation data	[73]
Austenitic stainless steels	2.3 x 10 <sup>-16</sup>	Least square fit to gas phase permeation data	[71, 74]

# Table 2-1: Effective hydrogen diffusion coefficients at room temperature for different steel types including the way in which they were determined

# 2.2.2. Ways to investigate the hydrogen interaction in a metal

Due to the intrinsic properties of a hydrogen atom, it is currently nearly impossible to visualise hydrogen directly in a metallic structure. Due to its small electron cloud, there is a lack of interaction with electron beams or X-rays. Therefore, electron diffraction, energy dispersive X-ray spectroscopy, X-ray diffraction, etc. cannot be used. Moreover, hydrogen is very mobile at room temperature in many metals increasing the difficulty to visualise hydrogen in the microstructure. Several approaches, however, exist to investigate the interaction between hydrogen and a metal.

# 2.2.2.1. Experimental methods

A. Hydrogen absorption, diffusion and trapping

The hydrogen solubility of a metal is usually determined by increasing the temperature and measuring H<sub>2</sub> with a suitable detector after it has left the metal. The most commonly used method to evaluate the hydrogen concentration and investigate the influence of hydrogen trapping is thermal desorption spectroscopy (TDS). With this technique, hydrogen desorption is measured as a function of temperature. TDS is stated to have the ability to investigate hydrogen trapping at different microstructural features and defects such as grain boundaries, dislocations and carbides [75, 76]. Desorption activation energies are typically determined by the Kissinger equation [77] by performing TDS measurements at different heating rates as first discussed by Lee and co-workers [58, 78].

Hydrogen permeation is a widely used technique to study hydrogen diffusion and trapping in a metallic membrane. The system comprises of two separated cells at both sides of the metal membrane. Hydrogen is produced electrochemically or via a gas phase in the first compartment, absorbs in the membrane, diffuses through the membrane and desorbs again in the second compartment. After a certain breakthrough time, the permeation current increases until a steady state is reached [79]. The technique is very sensitive and it may be difficult to compare results across different studies.

Internal friction experiments offer a possibility to estimate hydrogen diffusion as well since a Snoek-like relation was observed in hydrogen-containing austenitic steels caused by elementary jumps of hydrogen in the lattice. The relaxation enthalpy equals the hydrogen migration energy. The technique is able to distinguish lattice diffusion from the interaction with numerous traps [80].

An indirect way to visualise hydrogen on the surface, is the hydrogen microprint technique. A specimen is put in a solution containing silver ions. When hydrogen reaches the surface, it oxidises by the reduction and precipitation of a silver ion. The position of the silver atoms on the metal surface can be related to the preferred microstructural locations for hydrogen accumulation through SEM observation [81]. The technique is, however, unable to provide 3D information [82]. The silver decoration technique uses a similar principle, however, a different electrolyte is used. While the hydrogen microprint technique is executed in a AgBr emulsion, the silver decoration technique makes use of an aqueous solution of KCN and

AgNO<sub>3</sub> [83]. Alternatively, autoradiography provides a way to detect radioactive compounds in a photographic emulsion. Since hydrogen is not radioactive, tritium can be charged to metals, e.g. by electrochemical charging at room temperature. The radiographic emissions from tritium trapped inside the metal become visible in the photographic emulsion after some exposure time. TEM is used complementary to measure the autoradiograph (submicron level resolution) [84]. Scanning kelvin probe force microscopy (SKPFM) has also been used to visualise hydrogen at the surface with the use of a palladium coating. The visualisation is based on a change in potential of the Pd coating under the presence of hydrogen. The technique was for example successful in visualising differences in hydrogen diffusion between the ferrite and austenite phase of a duplex stainless steel [85].

Neutron diffraction might be a possibility to visualise hydrogen directly as a hydrogen atom is able to scatter neutrons in an appreciable amount [86]. The technique is, however, not readily available in many laboratories. Moreover, the technique is very difficult to control due to its limited interaction [82]. Small-angle neutron scattering was able to visualise hydrogen trapping at NbC in steel as enhanced neutron scattering was locally observed. The enhanced scattering disappeared after hydrogen desorption [87]. Secondary ion mass spectrometry (SIMS) is a method in which a specimen is irradiated with an ion beam leading to the emission of ions from the specimen subsequently analysed by a mass spectrometer. The technique is able to analyse hydrogen in a small area of several micrometre, digging into the specimen [88]. Nanoscale secondary ion mass spectrometry (nano-SIMS) is also stated to be able to visualise local distributions of hydrogen atoms although difficulties arise with distinguishing trapped hydrogen from atmospheric hydrogen [89].

Atom probe tomography (APT) was successfully used to visualise deuterium trapping in a material containing  $V_4C_3$  [90]. The APT technique uses electric fields to evaporate atoms. A time-of-flight detector determines the mass-to-charge ratio of the evaporated atoms and relates it back to their original position. Deuterium guarantees that the detected atoms entirely originate from the microstructure and not from the surrounding atmosphere [91].

# B. Mechanical properties and deformation mechanisms

The evaluation of the HE sensitivity is usually obtained through constant extension rate tensile testing and constant load testing. Since hydrogen embrittlement occurs only in certain temperature and strain rate ranges, these parameters should be carefully selected [82]. Mechanical testing is usually accompanied by fractography and microstructural analysis to evaluate the influence of hydrogen on fracture and deformation mechanisms.

The nano-indentation technique mechanically investigates small volumes of material and is able to perform measurements within a single grain. It is therefore possible to study the dislocation nucleation event with this technique. Three stages can be considered in the loading process: elastic loading, an

excursion in depth at the onset of plasticity and continued plastic loading. The technique can be applied to hydrogen precharged specimens or with in-situ electrochemical hydrogen charging.

In scanning and transmission electron microscopy, specimen holders have been developed for the observation of the effect of temperature, deformation and an environment (gaseous or chemical). As such, it was possible to conduct in-situ straining of a metal in a hydrogen-containing environment allowing hydrogen embrittlement to be evaluated. The limited hydrogen pressure and possible surface effects should, however, be considered carefully upon interpretation of these in-situ results [92, 93, 94, 95].

# 2.2.2.2. Modelling approach

Density functional theory (DFT) has been used to study the interaction between hydrogen and metals. In the atomistic simulations, a certain atom arrangement is created and it is subsequently determined whether this arrangement is favourable to occur. The preferential interstitial lattice sites for hydrogen were for example determined for the different iron lattices through DFT calculations in [55]. Moreover, the interaction of hydrogen with vacancies in FCC iron was studied in [96]. The interaction of hydrogen with carbides was investigated through first-principle studies as well, e.g. [97]. Due to the extensive calculation cost, large scale defects such as dislocations, grain boundaries or interfaces are not well studied yet.

To treat the interaction of hydrogen with larger defects, semi-empirical methods must be used such as the embedded atom method for molecular dynamic simulations [98]. Ab-initio calculations can, however, be regarded as more accurate and reliable depending on the type of interatomic potential used in the molecular dynamics simulations. These simulations can provide insights in the atomic processes reaching up to 10<sup>9</sup> atoms while only several hundreds of atoms are studied with ab-initio methods.

For simulations of the macroscopic scale, finite element methods have been used extensively to examine large-scale material properties. Continuum descriptions of hydrogen diffusion and trapping are for example well established and there are numerous examples in literature implementing them using finite element methods, e.g. [99]. Finite element analysis is also frequently used for modelling of the mechanical response in the presence of hydrogen [100, 101]. Recent developments in modelling focusses on coupling of macroscopic continuum models with accurate atomistic simulations. The binding energies of hydrogen atoms to dislocations and grain boundaries are for example calculated with DFT and incorporated into large-scale crystal plasticity finite element phase field models [102].

# 2.2.3. Hydrogen embrittlement mechanisms

The fundamental mechanism explaining hydrogen embrittlement in metals was already extensively debated on. A lot of controversy still exists resulting in multiple possible candidate mechanisms to date. In the following sections, the main mechanisms are elucidated and the supporting evidence is discussed.

# 2.2.3.1. Hydrogen-enhanced decohesion (HEDE)

In 1926, Pfeil [103] suggested that hydrogen had a remarkable weakening effect on intercrystalline boundaries. Moreover, hydrogen was stated to reduce the cohesion across cubic cleavage planes. Troiano [104] stated in 1959 that a weakening of interatomic bonds was involved with charge transfer between hydrogen and iron atoms. Oriani and co-workers [105, 106] quantitatively developed the hydrogen-enhanced decohesion or HEDE mechanism. A significant hydrogen concentration reduces the cohesive force of the iron lattice. Hydrogen is driven towards crack tips by the effect of the elastic stress field (stress-driven diffusion). As such, hydrogen accumulation at the crack tip can locally lower the cohesive strength resulting in faster propagation of cracks knowing that a crack grows when the local tensile elastic stress at the crack tip equals the local cohesive force of the lattice.

Several modelling strategies have provided proof for this mechanism. Recently, the effect of hydrogen on the cleavage strength across two {111} crystal planes in magnetic bcc a-iron was found to reduce from 30 to 22 GPa by thermodynamic-kinetic continuum and cohesive zone modelling [107]. A number of DFT studies provide evidence for the decohesion of grain boundaries, e.g. [108, 109]

The HEDE model lacks of experimental proof since there are no techniques available for the observation of events at the atomic level. A seemingly featureless fracture surface observed with SEM might still show shallow dimples that cannot be resolved with SEM. A possible proof is the easier field-evaporation of surface atoms during field-ion microscopy using hydrogen as imaging gas [57, 110]. Moreover, the observed reduction in crack-tip opening angle with increasing hydrogen concentration could also be regarded as proof for the decohesion model [82].

# 2.2.3.2. Hydrogen-enhanced localised plasticity (HELP)

The concept of hydrogen enhancing the plasticity in metals was first proposed by Beachem [111] in 1972. The author stated that the presence of sufficiently high hydrogen concentrations aids whatever deformation process the microstructure allows. Birnbaum and co-workers further expanded the concept and concluded that solute hydrogen reduced the elastic interactions between dislocations and elastic centres acting as barriers, as illustrated by the dislocation pile-up in Figure 2-16 [112]. The equilibrium situation of the dislocation pile-up is shown in black. When hydrogen gas was added in the environmental TEM, a new equilibrium was attained with the dislocations located closer together as indicated in white. The numbers represent the same dislocation.

# Chapter 2



# Figure 2-16: Composed image of a dislocation pile-up at a grain boundary without hydrogen (black) and with 95 torr (≈ 12.7 kPa) hydrogen gas (white) visualised with in-situ TEM in AISI 310S austenitic stainless steel [112]

The HELP mechanism further builds upon a high hydrogen concentration at crack tips due to hydrogen diffusion towards the elastic stress field at the crack tip and the absorption of hydrogen at the crack tip. Hydrogen subsequently facilitates dislocation activity at the crack tip localising the deformation. Crack growth then occurs through more localised microvoid coalescence.

Evidence for the HELP mechanism can be found in elasticity theory suggesting that dislocations are shielded from the full repulsive forces between them in the presence of hydrogen. Moreover, atomistic simulations have shown that hydrogen reduced the dislocation core energy and therefore also reduced the required stress for dislocation movement. Nano-indentation in the presence of hydrogen provides evidence for the HELP mechanism as well. Hydrogen lowered the indentation load at which dislocations nucleated. Moreover, a larger distribution of slip steps from other slip systems was present after indentation with hydrogen [113]. Moreover, a more confined plastic zone was observed in the hydrogen charged condition proving that hydrogen enhanced dislocation motion and reduced the distance between dislocations in pile-ups [114]. Internal friction experiments on hydrogen charged austenitic steels were interpreted within the HELP mechanism. Hydrogen decreased the start stress of localised plasticity and increased the mobility of the formed dislocations [115]. The correlation that was found between the amount of mobile hydrogen, i.e. hydrogen trapped at dislocations, and the severity of the hydrogen-induced mechanical degradation additionally supports the HELP mechanism [60].

# 2.2.3.3. Adsorption-induced dislocation emission (AIDE)

Lynch [116] suggested that hydrogen adsorption at the crack tip was responsible for crack growth. The reasoning was based on observations with crack velocities that are too high for hydrogen diffusion to be able to follow the crack propagation. At the crack tip, localised plastic flow takes place since hydrogen adsorption facilitates the emission of dislocations from the crack tip. The formation of a dislocation and surface step occurs through the breaking and reforming of interatomic bonds where adsorbed hydrogen facilitates this process by weakening the interatomic bonding. Nucleation and growth of microvoids ahead

of the crack tip is also involved in the crack propagation since the stresses ahead of the crack tip are sufficiently high. Within the AIDE mechanism, hydrogen diffusion to and adsorption at the crack tip is a prerequisite.

Supporting evidence for an embrittlement mechanism involving adsorption-induced localised slip processes can be found in the higher hydrogen concentrations at the surface and sub-surface compared to normal interstitial lattice sites, cf. Figure 2-14, atomistic simulations of dislocation emission from crack tips as well as indirectly from the observation of hydrogen-assisted cracking when diffusion cannot keep up with the crack propagation velocity [57].

# 2.2.3.4. Hydrogen-enhanced strain induced vacancies (HESIV)

Nagumo [117] proposed that hydrogen enhanced the creation of vacancies and their clustering during straining as such reducing ductile crack growth resistance. The authors compared the void density after an equal amount of fatigue cycles for both a hydrogen charged and uncharged nickel and iron alloy. They observed an increase in the void density in the presence of hydrogen. The link to hydrogen enhancing strain induced vacancies was made since the coalescence of vacancies leads to microvoids which can grow to larger voids upon the addition of more vacancies. McLellan et al. [118] also concluded that hydrogenating at 300 K resulted in a large abundance of vacancies compared to the non-hydrogenated specimen through TEM measurements studying the presence of Frank dislocation loops.

The HESIV mechanism further includes the formation of a high density of voids at crack tips due to the presence of a high hydrogen concentration that diffuse to and accumulate at the crack tip. Due to this large amount of voids in front of the crack, the matrix has a lower stress-carrying capacity and the onset of plastic instability occurs earlier. The most important direct evidence for the HESIV mechanism was provided by positron lifetime measurements. It was shown directly that hydrogen enhanced the creation of vacancies and promoted clustering of vacancies [119].

# 2.2.3.5. Stress-induced hydride formation

In the stress-induced hydride formation mechanism, crack propagation is aided by the repeated formation and cleavage of highly-brittle hydrides at the crack tip. The hydrides precipitate when the solubility of the lattice is exceeded, typically at regions with high stresses. The presence of hydrides creates additional stress concentrations which attract even more hydrogen [120]. The mechanism is accepted as one of the most important embrittlement mechanisms for metals exhibiting stable hydride structures such as zirconium or titanium. In general, the iron-based hydride is not stable at room temperature. In Fe<sub>50</sub>Ni<sub>50</sub>-"Mn<sub>x</sub> alloys, an FCC hydride phase was observed upon subjecting the alloys to electrochemical hydrogen charging [121]. No stress-induced hydride mechanism was, however, proposed for iron-based alloys.

# 2.2.3.6. Low-energy dislocation nanostructure mechanism

Recently, a new mechanism was proposed to explain HE based on ordered strain raisers controlling dislocation nucleation. Hydrogen-rich materials show the formation of low-energy dislocation nanostructures in the neighbourhood of strain raisers (carbides, inclusions, crack tips,...). These nanostructures act as sinks for hydrogen as such accumulating large amounts of hydrogen which increases the crystallographic misorientation as measured with TEM and favours cracking. The authors state that their proposed mechanism demands refocusing of the materials scientist's attention to delaying or inhibiting the formation of hydrogen-assisted dislocation nanostructures [122].

Figure 2-17 depicts a schematic illustration by the authors of different HE mechanisms. The left image shows the established mechanisms where atomic hydrogen interacts with dislocations (HELP), promotes decohesion at grain boundaries (HEDE), leads to the formation of clusters of vacancies (voids) (HESIV), interacts with precipitates, etc. The right image illustrates the low-energy dislocation nanostructure mechanism where hydrogen diffuses to crack tips increasing locally its concentration. The increased hydrogen concentration promotes dislocation cell formation with increasingly small dislocation cell sizes and increasing dislocation cell misorientation. Upon reaching a critical level, this causes further crack propagation [122].



Figure 2-17: Multiscale depiction of hydrogen embrittlement [122]: the left image shows the established hydrogen embrittlement mechanisms, the right image shows the newly proposed mechanism based on low-energy dislocation nanostructures

# 2.2.3.7. Combination of mechanisms for a better representation of reality?

Several authors proposed that a combination of the mentioned HE mechanisms could better explain the experimental observations. Dislocations that are emitted from crack tips as proposed by the AIDE mechanism could for example migrate more easily away from the crack tip due to the HELP mechanism. This could then ease the nucleation of new dislocations from the crack tip. When cracks propagate through the HELP, AIDE or HESIV mechanism, the propagation could be aided by HEDE occurring at particle/matrix interfaces or grain boundaries located in the crack propagation path. Nagao et al. [123] combined for example the HELP and HEDE mechanisms to a hydrogen-enhanced and plasticity-mediated decohesion mechanism for steels with a lath martensite microstructure. An attempt was made to unify a large number of research studies in a review paper that clearly pointed out the synergistic influence of HE mechanisms. It was stated that at low hydrogen concentrations, plasticity mediated mechanisms dominate (HELP, HESIV, AIDE) while once a critical hydrogen concentration is reached, the HEDE mechanism dominates HE [124].

The HELP and HESIV mechanisms are often combined as well. Martin et al. [125] performed fractography analysis and TEM beneath a quasi-cleavage fracture surface as typically observed for hydrogen-charged and fractured metals. It was proposed that voids and microcracks form at intersections of slip bands and propagate along these slip bands. The role of hydrogen is to enhance slip band formation (HELP), to lower the stress for void nucleation and to accelerate void growth (HESIV). Neeraj et al. [126] also proposed a combination of the HELP and HESIV mechanism to explain the fracture behaviour of pipeline steels. Kirchheim [127] translated the observations of the HELP and HESIV mechanisms to the defactant concept which provides a thermodynamic framework. In this defactant concept, trapped solute atoms lower the defect formation energy. The energy barrier for the generation of dislocation loops and/or vacancies is as such lowered.

#### 2.2.4. Specificities of hydrogen interaction with austenitic steels

As was explained in 2.2.1, the FCC crystal structure of austenitic steels is characterised by a largely different hydrogen solubility and diffusivity compared to BCC steels. The extremely low hydrogen diffusivity impacts the hydrogen embrittlement sensitivity in a positive way [128]. Due to the low hydrogen permeability, austenitic steels are able to sustain relatively long in a hydrogen environment. Nevertheless, brittle fracture was also observed for austenitic steels in the presence of hydrogen and differences in hydrogen diffusivity between austenitic steels impact the HE resistance. With internal friction measurements, it was found that alloying with chromium, manganese or molybdenum reduced the hydrogen mobility while nickel increased it. A correlation was found after mechanical testing between the effects of the alloying elements on the hydrogen mobility and the HE sensitivity [80]. Xiukiu et al. [74] stated, however, that the effect of alloy composition on the hydrogen diffusivity in austenitic statinless steels was not as significant as in BCC metals. A least square fit of the temperature dependent hydrogen diffusion coefficient D [m²/s] (cf. equation 2-17) for six types of austenitic stainless steels was found:

$$D = 5.76E-7 \exp(\frac{-53620}{RT})$$
(2-18)

As an alternative for the diffusion of hydrogen through the interstitial FCC lattice positions, enhanced hydrogen diffusion in the presence of dislocations has been mentioned. Pu et al. [129] demonstrated the phenomenon for a dislocation that migrated to the surface. Hydrogen trapped at the dislocation migrated to the surface along with the moving dislocation as illustrated in Figure 2-18. Takai et al. [130] measured the hydrogen evolution upon the application of plastic strain to 316L and 304 austenitic stainless steel. Hydrogen desorption increased rapidly when plastic deformation began which was explained by dislocations dragging hydrogen along with their movement. This phenomenon occurs when the dislocation velocity approached the hydrogen diffusion rate.



Figure 2-18: Hydrogen transport with moving dislocations in austenitic steels [129]

The microstructural complexity of austenitic steels after (improper) processing and/or during and after deformation largely impacts the interaction with hydrogen. Welding of austenitic steels could for example lead to the formation of a duplex microstructure (large amounts of ferrite). Ferrite acts as a fast diffusion path for hydrogen as the BCC structure is characterised by a higher hydrogen diffusivity, cf. 2.2.1. The HE sensitivity, therefore, increased with increasing ferrite content in duplex austenite/ferrite fusion welds [131].

Austenitic steels in which localised deformation is promoted were stated to correlate with greater susceptibility to hydrogen embrittlement. Deformation bands impinge at twin or grain boundaries or intersect with each other increasing the stress level at these locations and attracting hydrogen. Hence, at these stress concentrations, voids and microcracks can be formed. [132] The degree of localised deformation is for example dependent on the nickel content. A higher nickel content results in more homogeneous deformation which decreases the HE sensitivity [133]. As stated above, the addition of nickel at the same time increases the hydrogen mobility. The prediction of the effect of nickel addition is therefore not always straightforward.

The formation of a'-martensite during deformation of metastable austenitic steels has been a major concern for its HE sensitivity. Several authors reported that the most detrimental effect on the HE susceptibility of austenitic steel was the formation of a'-martensite upon deformation [134, 135, 136]. Figure 2-19 (a) shows the principle of the so-called hydrogen diffusion highway effect. The diffusivity of hydrogen in a'-martensite is orders of magnitude higher than the diffusivity in austenite. This means that when a'-martensite is present locally at the crack tip, the local accumulation of hydrogen at the crack tip is facilitated [137]. The strain-induced a'-martensitic transformation additionally causes problems with respect to hydrogen solubility. When the parent austenite phase transforms, the newly formed a'-martensite phase is supersaturated with hydrogen due to its lower hydrogen solubility. Hydrogen is then stated to diffuse to the austenite/a'-martensite phase boundary resulting in easier crack initiation [138]. The mechanism is illustrated in Figure 2-19 (b) [139]. It has also been shown that a higher strain-induced a'-martensite fraction does not always correlate to a higher embrittlement. Fatigue crack growth rates in hydrogen of cold worked AISI 301 and 302 ASS were similarly affected although the a'-martensite fraction was lower for the 302 ASS. The general distribution and fine particle size of the a'-martensite was stated to be more important than its fraction [140].



Figure 2-19: (a) Hydrogen diffusion highway effect due to the presence of a'-martensite in an austenitic matrix [141] (b) formation of a'-martensite from austenite leading to crack initiation at the interface [139]

The transformation of austenite to  $\epsilon$ -martensite was also held responsible for the HE sensitivity of austenitic steels by some authors. Inoue et al. [142] concluded that the main reason for HE in austenitic stainless steel was the presence of  $\varepsilon$ -martensite in the vicinity of crack tips and the subsequent propagation of cracks along the austenite/ɛ-martensite interface. The most important experimental support for claiming that  $\epsilon$ -martensite is responsible for HE is that the habit plane of the austenite to  $\epsilon$ martensite transformation is at the same time the most prone to hydrogen-assisted crack initiation [80]. Chun et al. [143] found that the hydrogen embrittlement sensitivity increased proportionally with the initial thermal ε-martensite fraction for high manganese steels. The austenite/ε-martensite interfaces were mainly responsible for severe hydrogen embrittlement. Alloying of austenitic steels with silicon, however, contradicts the claimed deleterious role of  $\varepsilon$ -martensite. Silicon lowers the SFE and promotes the formation of  $\varepsilon$ -martensite. Mechanical tests showed that the addition of silicon positively affected the ductility of hydrogen charged austenitic steels [80]. Teus et al. [144] also concluded that HE of austenitic steels was not correlated with the ε-martensite transformation. In fact, the transformation was claimed to retard localised slip which increased the HE resistance. Li et al. [145] state that the intermediate formation of  $\epsilon$ -martensite instead of the direct  $\gamma \rightarrow \alpha$ '-martensite transformation results in a more compatible strain evolution and hinders the nucleation and growth of hydrogen-assisted cracks increasing the resistance to HE. Koyama et al. [146] concluded that stable  $\epsilon$ -martensite had a smaller effect on hydrogen-induced degradation than metastable ɛ-martensite. Two negative roles and one positive role were proposed for the influence of  $\varepsilon$ -martensite on HE: (i)  $\varepsilon$ -martensite provides stress concentrations, (ii) the interface acts as a crack initiation site and (iii) the interface arrests crack propagation. In addition, an advantage over the a'-martensitic transformation is the low hydrogen diffusivity, which might even be lower than the hydrogen diffusivity of austenite [55].

Koyama et al. [147] performed TDS tests by cooling down instead of heating. As such, thermal martensitic transformation took place and the influence on hydrogen desorption could be evaluated. Both the a'-martensitic and  $\varepsilon$ -martensitic transformation induced hydrogen desorption. For the a'-martensitic transformation, the desorption was linked to the higher diffusivity of the BCC phase. Since the hydrogen diffusivity does not increase with the formation of  $\varepsilon$ -martensite, the enhanced desorption was associated with the motion of hydrogen decorated transformation dislocations.

To study the influence of prior cold work on the hydrogen distribution in austenitic steels, Enomoto et al. [148] performed TDS tests after gaseous hydrogen charging of 304 and 316L austenitic stainless steel. Their results are presented in Figure 2-20. A gaseous charging procedure consisting of exposure to a hydrogen atmosphere of 98 MPa at 250°C for 3 days was performed. A uniform distribution of hydrogen was reached in the specimen. The influence of cold work on 316L was negligible for both prestrain levels while for 304, 40% prestrain had a significant influence. The observations could be linked to the larger metastability of 304 since the presence of large amounts of a'-martensite both reduced the average hydrogen solubility and increased the average hydrogen diffusivity of the austenitic steels. The higher

fraction of dislocations and vacancies due to cold work did not influence the hydrogen diffusivity in austenitic steels which is in strong contradiction with the effect of increased dislocation density and vacancy concentration on the hydrogen diffusivity in ferritic steels [60].



Figure 2-20: Thermal desorption spectroscopy data for austenitic stainless steel type 304 and 316L after gaseous (98 MPa, 250°C, 3 days) hydrogen charging. Different amounts of prestrain were induced [148]

Based on the previously mentioned observations, it could be argued that the austenite stability and SFE can be considered as important parameters for the prediction of the HE sensitivity of austenitic steels. Izawa et al. [149] found for instance a correlation between the M<sub>d30</sub> temperature and the relative reduction in area for the AISI 300 series austenitic stainless steels. However, the stability of austenite alone does not explain HE. The presence of martensite is not a sufficient nor a necessary condition for HE to occur [150]. Moreover, it has also been stated that HE susceptibility does not correlate with the SFE despite the influence on homogeneous deformation since different steels with similar SFEs showed largely different susceptibilities to hydrogen [133].

Hydrogen itself is also stated to influence the deformation features that are formed. In general, more slip planarity was observed in the presence of hydrogen. Ulmer et al. [151] observed strain localisation in AISI 304 and 310 stainless steel under high hydrogen concentrations. Nibur et al. [132] observed deformation localisation in the form of slip bands in austenitic forgings. A possible reason is a reduction of the stacking fault energy of FCC metals by hydrogen. This was shown both through ab initio studies in aluminium [152] and through experimental work. Pontini et al. [153] measured a 37% SFE reduction in AISI 304 austenitic stainless steel by XRD measurements and Robertson [154] found a 20% reduction in SFE in AISI 310 austenitic stainless steel by in-situ TEM measurements. The latter author reported, however, that a 20% reduction will not increase the separation between partial dislocations in such a way that cross-slip will be affected for this type of austenitic stainless steel. Apart from the reduction in SFE, a second reason exists for the enhanced slip planarity in the presence of hydrogen. Hydrogen influences the dislocation character. It preferentially stabilises edge segments of dislocations inhibiting them from cross-slipping. The corresponding observations were done by in-situ deformation of high-purity aluminium in a gaseous hydrogen environment [155].

In materials prone to deformation twinning, an influence of hydrogen was observed as well given the link with the SFE. The hydrogen-enhanced densified twinning (HEDT) mechanism was proposed based on the study of Fe-22Mn-0.6C TWIP steel. EBSD and TEM observations were performed at different prestrain levels with and without hydrogen presence during straining. Hydrogen reduced the twin thickness and increased the number of nucleation sites. As a result, the twin volume fraction in the hydrogen charged specimens was higher than in the hydrogen free specimens. The twin spacing was gradually reduced as well. Figure 2-21 schematically illustrates the influence of hydrogen on twinning at different stages. During the nucleation stage, hydrogen increases the distance between partial dislocations and as such eases twin nucleation. The increased amount of nucleation sites, reduced twin thickness and twin spacing are illustrated in the growth and stable stage [156].



Figure 2-21: Schematic illustration of the hydrogen-enhanced densified twinning mechanism: (a) nucleation stage, (b,c) growth stage, (d,e) stable stage [156]

Koyama et al. [157] summarised the effects of hydrogen on the deformation-induced  $\varepsilon$ -martensite transformation. Hydrogen was shown both to promote [158] and to suppress [159] the  $\varepsilon$ -martensitic transformation in literature. The latter being regarded as an unconventional hydrogen effect. Three insights were provided by the authors [157]: (i) hydrogen increases the critical stress for the nucleation of  $\varepsilon$ -martensite. This effect is obtained by (1) an increase in friction stress for transformation dislocations and (2) a decrease in thermodynamic driving force for the phase transformation, (ii) hydrogen promotes the dislocation-motion nucleation process because of its reduction of the stacking fault energy, (iii) hydrogen decreased the average thickness of  $\varepsilon$ -martensite plates. The latter two are similar as the observations for deformation twinning illustrated in Figure 2-21. The authors concluded that as a result, hydrogen promotes deformation-induced  $\varepsilon$ -martensite formation at similar plastic strains.

Several authors observed an increase in the a'-martensite fraction when hydrogen was present in the microstructure during straining [160, 161]. A possible explanation could be that an a'-martensite embryo is stabilised faster in the presence of hydrogen since hydrogen reduces the distance between dislocations in a pile-up, cf. Figure 2-16 [41]. Other authors mention, however, a decrease in the a'-martensite fraction in the presence of hydrogen during plastic straining [162, 163, 164, 165]. A possible explanation for a reduction in the a'-martensite fraction was proposed by Lu et al [162]. The reduction of the SFE by hydrogen hindering dislocation cross-slip was used for the explanation. The occurrence of intersections of different slip systems that can serve as nucleation sites for a'-martensite were stated to be less favoured in the case of limited cross-slip. Kim et al. [165] explained their observation of a reduced a'-martensite fraction in the presence of hydrogen by the destruction of short-range order. Strain-induced martensite is a disordered BCC phase created by moving dislocations destructing short-range order. Hydrogen suppression of strain-induced martensite formation thus corresponds to hydrogen-enhanced ordering. The loss in ductility of metastable austenitic steels was attributed to the lower fraction of martensite since the TRIP effect was less pronounced.

A significant amount of the evidence supporting the HELP mechanism was obtained for austenitic steels, cf. 2.2.3.2. The reduction in SFE was originally not part of the HELP mechanism. However, the enhanced planar slip due to the SFE reduction and/or change of the dislocation character by hydrogen contributes to the localised plasticity at regions with a high hydrogen concentration. It could also be noted that an alternative explanation for the observations was found through ab initio calculations of the electronic structure of austenitic steels [166]. Hydrogen increases the concentration of free electrons. It was shown that alloying elements that decrease the concentration of free electrons improve the hydrogen resistance of an austenitic steel. The calculations also indicated that hydrogen decreased the shear modulus which in turn decreased the stress for activation of dislocation sources as well as the line tension of dislocations increasing their mobility. Moreover, a decreased shear modulus also decreases the distance between dislocations in pile-ups. Their findings are thus an electronic version of the HELP mechanism. If one takes into account an inverse dependency of the SFE with the number of free electrons, this approach also confirms that hydrogen lowers the SFE of austenitic steels.

# 2.3. <u>Conclusions</u>

In this literature overview, the specific properties of austenitic steels exhibiting an FCC crystal structure were discussed. The different deformation mechanisms that can be present in FCC iron were discussed, i.e. dislocation processes, stacking fault formation, deformation twinning and strain-induced martensitic transformation. The mechanical properties vary largely depending on the operative deformation mechanism. Tuning of the chemical composition can largely improve the mechanical performance providing material solutions for various demanding applications.

Hydrogen embrittlement is a problem encountered in many metals. It is a complex material degradation phenomenon acting at different length scales. In many cases, a combination of the mentioned embrittlement mechanisms is required to explain the observed macroscopic brittle fracture behaviour. Moreover, the preferred occurrence of one mechanism over another is most likely dependent on the hydrogen concentration, dislocation density, applied strain rate, phase fractions, etc. Austenitic steels were found to suffer from a detrimental hydrogen effect as well despite their very low hydrogen diffusivity at room temperature. The different deformation mechanisms that can take place influence the hydrogen embrittlement sensitivity of austenitic steels. Moreover, the presence of hydrogen in the microstructure during deformation influences the deformation process itself. Contradictions can, however, be found on the martensitic transformation. Its role might be dependent on the specific material and experimental conditions.

Although an appreciable amount of literature was already published on the hydrogen interaction with austenitic steels, a lot of work still needs to be done. The current PhD aims amongst others at contributing to an increased knowledge on the following gaps:

- Literature currently lacks of temperature-dependent hydrogen diffusion coefficients for a variety of austenitic steels, in particular twinning-induced plasticity steels.
- The analysis of TDS data on austenite-containing steels is not well established yet. Largely diverging values can be found for desorption activation energies of hydrogen trapping sites.
- The effect of hydrogen on the operative deformation mechanisms should be investigated further, e.g. to clarify the mentioned contradictions with respect to the influence of hydrogen on martensitic transformations.

A more detailed positioning of the research performed in this PhD within the available literature can additionally be found in the introduction of the following chapters.

# Chapter 3 Experimental methods

#### 3.1. Introduction

Investigating the interaction between hydrogen and austenitic steels (FCC) brings along several challenges compared to the study of hydrogen interaction with BCC/BCT steels (ferrite, martensite). The challenges mainly arise due to the low hydrogen diffusivity at room temperature, which is, as stated in the introduction, in fact an intrinsic advantage for FCC steels since it reduces the hydrogen embrittlement sensitivity. The specimen thickness in previous research on BCC steels in our research group was typically 1 mm. A homogeneous hydrogen concentration was reached in several hours when using hydrogen charging methods at room temperature. As a comparison, Figure 3-1 gives a schematic illustration of the normalised hydrogen concentration profile in an austenitic specimen with a thickness of 1 mm after several charging times. More information on the used model will be given in chapter 4. A diffusion coefficient of 1E-16 m²/s at room temperature was assumed, i.e. a representative value for austenitic steels based on literature data [74]. It is clear that the hydrogen saturation time, i.e. the time to reach a homogeneous hydrogen concentration through the thickness, is orders of magnitude larger for FCC steels. A PhD of 4 years would even not suffice to reach the centre of the specimen. An alternative experimental methodology was thus needed that took into account the specific hydrogen properties of austenitic steels. Moreover, a methodology for the study of the alternative deformation mechanisms in FCC needed to be developed as well. This chapter summarises the experimental methodologies and the experimental methods used throughout this PhD. More details on research specific parameters will be given in the corresponding chapters.



Figure 3-1: Theoretical normalised hydrogen concentration profile after several charging times for a 1 mm austenitic steel sheet, D = 1E-16 m<sup>2</sup>/s at room temperature

# Experimental methods

# 3.2. <u>Microstructural analysis</u>

In order to better understand the hydrogen/microstructure interaction in FCC steels, a thorough characterisation of the microstructure was needed. For all alloys studied in this PhD, plate material was received. Several material conditions were investigated: the as-received condition, the hydrogen charged condition and after plastic deformation of the materials, both without and with hydrogen present during the deformation step. Several techniques were used to accomplish this, for which a general explanation is given in 3.2.1. The most important microstructural characterisation technique used in this PhD was electron backscatter diffraction (EBSD). A more detailed description on this technique is given in 3.2.2.

Standard metallographic preparation was first performed including mechanical cutting or water jetting (the latter was used for the more complex geometries), grinding, polishing, electropolishing and etching. A thickness reduction compared to the as-received plate thickness was accomplished by mechanical grinding. A constant thickness value was always aimed for with a maximal deviation of 0.01 mm. The used etchants and electropolishing parameters are specific for the studied material and will therefore be specified in the corresponding chapters.

# 3.2.1. Microstructural characterisation techniques

Optical microscopy served as starting point in the characterisation of the microstructure. It gave a first indication of the grain size and shape. A Keyence optical microscope (VHX-S90BE) was used in this dissertation. The software of the microscope was used to determine phase fractions based on differences in brightness between the phases.

Scanning electron microscopy (SEM) was performed for a more detailed visualisation of the microstructure. A FEI QUANTA FEG 450 SEM was used at an accelerating voltage of 20 kV and spot size of 5 nm. Secondary electron (SE) images were acquired in this PhD. SE originate from the inelastic interaction of primary electrons from the electron beam with the atoms of the specimen. The SE images give a topographical image of the surface region (up to 5 nm in depth).

Transmission electron microscopy (TEM) was performed when high resolution was needed for the characterisation of certain microstructural features, e.g. stacking faults or nanometre-sized carbides. The TEM studies were performed on a JEOL (JEM-2200FS) device operated with an accelerating voltage of 200 kV and a spot size of 1.5 nm. Thin foils with a thickness below 100 µm were prepared by mechanical grinding. These thin foils were subsequently electropolished.

X-ray diffraction (XRD) was performed to study the presence of different phases. XRD makes use of monochromatic X-rays that are focussed on a specimen. Diffraction of the X-rays subsequently occurs on the specimen's crystal lattice planes. A significant specimen volume can as such be analysed for the presence of different phases and strains. The XRD device made use of a Mo source and was operated at a voltage of 40 kV and a current of 40 mA. The angle 20 was scanned with a step size of 0.006° and 5 s holding time per step.

Energy dispersive X-ray spectroscopy (EDX) was used for elemental analysis of the specimens. The technique makes use of the characteristic X-rays that arise from the interaction between the primary electron beam of a SEM or TEM and the atoms of the specimen. When an electron is removed from one of the shells of an atom, the hole is filled by an electron from a higher shell. The difference in energy is compensated by the emission of a characteristic X-ray. The energy spectrum of the emitted X-rays is determined by the EDX detector and gives a representative determination of the chemical composition of microstructural features in the specimen.

A FMP30 Feritscope of Helmut-Fisher was used to calculate the fraction of magnetic phases in a relatively large volume (20 mm<sup>3</sup>) of the materials. The materials should have a thickness of 3 mm to obtain reliable results.

#### 3.2.2. Electron backscatter diffraction

EBSD is a SEM-based technique that is particularly powerful for the microstructural characterisation of crystalline materials, including grain size, grain orientation, phase constituents, boundary properties, strain determination and texture analysis. The technique makes use of backscattered electrons generated by the primary electron beam of a SEM that diffracted on specimen lattice planes. These backscattered electrons are detected by a phosphorous screen, as illustrated schematically in Figure 3-2. Positive interference is observed in the form of a Kikuchi patterns. These patterns are analysed and indexed in a fully automated way through an OIM data collection software that provides the crystallographic orientation data. The specimen is ideally tilted to an angle of 70° from the horizontal (20° from the primary beam) to allow for a large fraction of backscattered electrons. All scans were performed with a hexagonal scan grid. The step size of the EBSD measurements was chosen large enough to allow for a relevant specimen area to be tested without creating too large data file sizes. The lowest possible step size, i.e. 0.02 µm, was used when very detailed scans on small deformation features were searched for. When EBSD measurements were compared to evaluate differences between material conditions in a specific study, the step size was always taken equal to exclude differences due to the change of experimental parameters. Multiple EBSD measurements were performed on every condition to allow for verification of the observations. Martensite fraction, twin length and grain size were presented as an average value. Analysis of the crystallographic data was performed with dedicated software, i.e. TSL-OIM® Data analysis V7.3 software [167].

Several parameters deserve some attention:

The <u>image quality (IQ)</u> parameter describes the quality of a Kikuchi pattern. It is dependent on the material and its condition, however, it is also a function of the technique, sample preparation (surface roughness creates a deviation from the ideal 70° tilt for diffraction) and other external factors such as video processing (contrast and brightness). Most interesting in the present PhD, is its indication of imperfections in the crystal lattice. A grain boundary comprises for example of a mix of two patterns of the neighbouring

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grains which leads to a low image quality. The uniformity of deformation can also be investigated by plotting this parameter for a certain scanned area by creating an image quality map.



Figure 3-2: Kikuchi diffraction in the SEM [168]

The <u>confidence index (CI)</u> is a parameter calculated by the software. A detected diffraction pattern can fit with several possible orientations. The software ranks these orientations with a voting system. The confidence index is typically a number between 0 and 1, although -1 is ascribed to patterns that could not be indexed. The higher the CI value, the more certain it is that the pattern was correctly indexed. One should, however, be careful when a CI of 0 was given, since this simply means that two options are equally probable. The pattern could nevertheless still be correctly indexed [169]. When presenting images of an EBSD scan in this PhD, points with a CI below 0.1 were always excluded (indicated in black). The 0.1 threshold was defined based on the CI study by Field [170].

A <u>phase map</u> gives a graphical representation of which phase was measured at every scanned point as diffraction patterns are characteristic for the crystal structure. It allows for visualisation of the distribution of different phases in a microstructure as well as the determination of the phase fraction (area fraction).

A <u>pole figure (PF)</u> shows the crystal direction as a function of the macroscopic reference system. The crystal orientation can be extracted from the diffraction pattern as well. For plate material, the macroscopic reference system typically comprises of the rolling direction (RD), transverse direction (TD) and the normal direction (ND). Figure 3-3 shows an example of a <001> pole figure for a cubic crystal. The three red points indicate three equivalent planes in the crystal. The open circles correspond to points extending into the bottom half of the sphere.

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Figure 3-3: Illustration of the construction of a pole figure [169]

An <u>inverse pole figure (IPF)</u> shows the macroscopic sample directions relative to the crystal reference frame. A schematic illustration is given in Figure 3-4 (a) for a cubic lattice. A unit triangle (Figure 3-4 (b)) can be extracted from this inverse pole figure, containing only one representation of the macroscopic normal direction. This unit triangle is typically used as a legend, coloured in a rainbow pattern, to create IPF maps. For a cubic lattice, this legend is illustrated in Figure 3-4 (c). On an IPF map, the orientation of a certain macroscopic direction is presented for every scanned point relative to the crystal reference system allowing for the identification of grains. Point located in the same grain are characterised by more or less the same crystallographic orientation with a maximal misorientation of 5°. In this work, the presented IPF maps were always constructed based on the ND of the steel samples.



Figure 3-4: Illustration of a normal direction (ND) inverse pole figure (a) including the unit triangle representation (b), legend of an ND IPF map based on the unit triangle (c) [169]

Extracting <u>grain boundaries</u> from EBSD data is a possibility as well. High angle grain boundaries (HAGB) are typically defined as grain boundaries with a misorientation above 15°, while low angle grain boundaries (LAGB) have a misorientation between 5° and 15°. Several special boundaries exist as well. A twin boundary in FCC steels is characterised by a 60° rotation about a <111> crystal direction, i.e. the first of two criteria that define a twin. The OIM software will automatically investigate this first criterion. A twin boundary is then identified if the misorientation across the boundary lies within 5° from this specified misorientation, e.g. 60.7° about a <10 10 11> axis could be considered a twin [171]. Since an EBSD scan is a 2D measurement, the twin boundary plane cannot be confirmed from an OIM scan. The second criterion that defines a twin boundary, i.e. the twinning plane, can thus not be verified in a straightforward way.

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#### 3.3. <u>Hydrogen charging and detection</u>

Literature on hydrogen charged FCC steels includes both gaseous and electrochemical hydrogen charging. Gaseous charging can be applied at elevated temperatures and pressures which can significantly reduce the time needed to saturate an austenitic steel since the diffusion coefficient increases with increasing temperature. The temperatures at which electrochemical charging can be performed are more limited due to evaporation of the electrolyte. Electrochemical charging is, however, safer to apply as making use of high temperatures and pressures includes risks. The flammability of hydrogen gas also implicates additional safety measures.

Throughout the present work, <u>hydrogen charging</u> was mostly done electrochemically. The specimen acted as the cathode, while platinum foils present at both sides of the specimen acted as anode. The electrochemical charging conditions for austenitic steels should not be too severe to account for the low hydrogen diffusion coefficient. If hydrogen is not able to diffuse to the bulk of the specimen at a sufficiently high speed, a too high hydrogen concentration will accumulate in the near surface region causing damage [172]. Unless stated otherwise, an electrolyte of 0.5M H<sub>2</sub>SO<sub>4</sub> was used in this work. Thiourea (CH<sub>4</sub>N<sub>2</sub>S, 1 g/L) was added as a poison for the hydrogen recombination reaction. This electrolyte was already used extensively in the research group for electrochemical charging of BCC steels, e.g. [173, 174]. Multiple electrolyte solutions were compared in terms of efficiency and absence of damage prior to the selection for hydrogen charging of FCC steels [175, 176]. A constant current density of 0.8 mA/cm<sup>2</sup> was applied, i.e. charging was done galvanostatically. This value was low enough to avoid hydrogen-induced cracking on the specified in the following chapters.

A Galileo G8 set-up was used for <u>hydrogen detection</u>. The set-up consists of two different furnaces to control hydrogen desorption, i.e. an impulse furnace and an infrared furnace. Hydrogen detection is possible via two different detectors, i.e. a thermal conductivity detector and a mass spectrometer. The thermal conductivity detector consists of two gas channels. One of the channels contains a pure carrier gas (N<sub>2</sub>) while the other channel contains carrier gas and measuring gas (H<sub>2</sub>). The thermal conductivity of both gas phases is measured by thermistors. The difference in thermal conductivity is proportional to the H<sub>2</sub> content of the measuring gas [177]. The mass spectrometer works with a carrier gas (N<sub>2</sub>) as well. The gas is ionised and the ions are separated based on their mass-to-charge ratio. The device makes use of a transmission quadrupole coupled to a secondary electron multiplier detector. Only ions with a predefined mass-to-charge ratio will reach the detector by travelling through the quadrupole. The detector transforms the ions to a secondary electron signal which is multiplied to a measurable signal [178]. Calibration of the devices was always executed with forming gas (5% H<sub>2</sub> in N<sub>2</sub>). Several fixed volumes of the forming gas were injected in the furnace and analysed by the detector of interest resulting in a calibration factor. The calibration was repeated every time tests were performed (day based) or every time

a different combination of furnace and detector was made. In the following sections, the different test procedures that were executed with these furnaces and detectors are explained in more detail. When evaluating the hydrogen concentration/distribution with any of the subsequently mentioned procedures, the time in between hydrogen charging and sample insertion in the furnace was kept to exactly 1 minute to obtain a consistent test protocol.

# 3.3.1. Melt extraction

The total hydrogen concentration present in the specimens was evaluated through melt extraction. The impulse furnace was used for heating to 1600°C which is above the melting temperature of the steels used in this work. The thermal conductivity detector was used for hydrogen detection. The technique was mainly used to evaluate the hydrogen concentration as a function of charging times since this gave valuable information on the hydrogen diffusion speed and saturation level. The specimen geometry was rectangular with dimensions of 8x6 mm<sup>2</sup>. As the thickness varied depending on the performed research, this will be specified in the following chapters.

#### 3.3.2. Hot extraction

To measure the hydrogen concentration that leaves the specimen at a constant temperature below its melting temperature, the infrared furnace was used (temperature  $\leq$  950°C). In this type of experiment, typically termed hot extraction, the furnace was again coupled with the thermal conductivity detector allowing for comparison with the total hydrogen concentration as determined through melt extraction. The diffusible hydrogen concentration is typically determined by hot extraction experiments at a temperature of 300°C [179]. However, 900°C was also relevant in this work since this coincides with the maximum temperature in TDS (see next section). The specimen geometry was circular with a diameter of 20 millimeter. The thickness varied again depending on the material and will be specified in the following chapters.

# 3.3.3. Thermal desorption spectroscopy (TDS)

Thermal desorption spectroscopy (TDS) is an experimental procedure used to assess the distribution of hydrogen within a metallic crystal lattice and its imperfections [180]. The infrared furnace was used since it can gradually heat a specimen at a fixed heating rate from room temperature to 900°C. Different heating rates are typically used to be able to extract activation energies which will be further specified in the following chapters. The specimen geometry for the TDS tests was also circular with a diameter of 20 millimeter. The thickness will be specified in the following chapters as well. Hydrogen that desorbs from the specimen could continuously be detected by the mass spectrometer. This method allowed for the visualisation of hydrogen desorption as a function of temperature rather than yielding one value for the hydrogen concentration as was the case for melt and hot extraction making use of the thermal conductivity detector.

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#### 3.4. Tensile testing

As hydrogen has a pronounced influence on the mechanical properties of metals, mechanical testing comprised an important part of the experimental work in this PhD. Constant extension rate tensile tests were performed in which the extension rate was chosen depending on the intended output, as further specified in the different chapters dealing with mechanical degradation. Throughout the entire PhD, an Instron 5800R electro-mechanical tensile bench was used.

#### 3.4.1. Procedure and set-up

Reference tests were mostly performed in air. For specific cases, the reference tests were performed in a solution (demineralised water) to better mimic the test conditions with electrochemical hydrogen charging (cf. Chapter 7). Different approaches were used for the tests including hydrogen charging. The tests were either executed in-situ, i.e. with continuous electrochemical hydrogen charging during the test, or ex-situ, i.e. in air with hydrogen internally present in the microstructure. For both options, electrochemical hydrogen precharging was performed, for which the charging time depended on the specific investigation that was performed. Saturation, i.e. a homogeneous hydrogen distribution through the specimen, via electrochemical charging was never aimed for in the case of tensile testing (cf. Figure 3-1). The stress and strain level were determined using the concepts of engineering stress and strain. For the engineering stress, the software documented the forces applied to the specimen which were subsequently devided by the initial cross-sectional area of the specimens. Due to the limitations in measuring the material strain accurately when an in-situ charging set-up surrounds the specimen, the engineering strain of the specimen was always evaluated by the crosshead displacement:

$$\varepsilon = \Delta L/L_0 \tag{3-1}$$

With  $L_0$  the initial gauge length [m] and  $\Delta L$  the crosshead displacement [m].

To evaluate the embrittling effect of hydrogen, an average embrittlement index (EI) was calculated based on the fracture elongation of the reference and hydrogen charged tests. This allowed to qualitatively compare the susceptibility to HE for different material conditions. The parameter was defined as followed:

$$EI = \frac{av.elongation ref. - av.elongation H}{av.elongation air} x 100 [\%]$$
(3-2)

The EI varies between 0 and 100%, with 0% meaning that there is no ductility loss and that the material is insensitive to hydrogen. When an EI is 100% is reached, HE is maximal. A deviation (Dev) on the average EI was calculated as well. For this value, the maximal and minimal EI value was calculated based on the available data:

$$Dev = \frac{EI_{max} - EI_{min}}{2} \times 100 \ [\%]$$
(3-3)
In a similar way, the loss (%) in ultimate tensile stress was calculated and compared for different material conditions.

Figure 3-5 schematically presents the in-situ tensile test cell that was designed in this PhD for tensile tests on low hydrogen diffusivity materials. The previously used in-situ cell was downscaled to be able to use smaller specimen sizes which could be used in the electrochemical charging set-ups for hydrogen precharging. As such, multiple specimens could be precharged at the same time and be transferred to the in-situ cell when precharging was completed. The cell consists of a cylinder which is covered at both sides. O-rings guaranteed sufficient sealing to prevent leakage. A platinum grid was added surrounding the tensile specimen to act as counter electrode for the in-situ electrochemical hydrogen charging. A connection was point welded to the platinum grid and brought to the exterior of the cell through a predrilled hole. The electrical connection with the specimen was accomplished outside the cell as well.



Figure 3-5: Schematic representation of the in-situ tensile test cell

The tensile geometry of the specimens used for in-situ testing is given in Figure 3-6. This geometry was chosen based on the work of Koyama et al. [181]. The asymmetric grips were designed to compensate the additional aluminium cover at the bottom of the in-situ cell. For ex-situ tensile tests, the same gauge section was used, however, the length of the grips was slightly reduced since no electrochemical cell was needed to surround the specimens during tensile testing, as indicated in Figure 3-7. When tensile tests were performed ex-situ, specimens were transported to the tensile bench within two minutes after the

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charging procedure was stopped. In-situ tests took five minutes to mount the specimen in the in-situ cell. Before the start of the in-situ tensile tests, the specimen was charged inside the cell for five minutes to compensate for the loss of hydrogen during the transfer from the precharging cell to the tensile cell.



Figure 3-6: Tensile specimen geometry for in-situ tensile tests (dimensions in millimeter)



Figure 3-7: Tensile specimen geometry for ex-situ tensile tests (dimensions in millimeter)

The tensile tests were executed in a smaller electrolyte volume (100 ml) than the volume used for precharging (500 ml). 2205 duplex stainless steel with a thickness of 1.35  $\pm$  0.01 mm was used to test whether this did not influence the performance of the charging procedure. Tests were performed for 2 hours in the H<sub>2</sub>SO<sub>4</sub> electrolyte solution at a current density of 0.8 mA/cm<sup>2</sup>. Figure 3-8 clearly illustrates that equal levels of hydrogen were absorbed in the steel despite the electrolyte volume being smaller.



Figure 3-8: Hydrogen concentration (wppm) in 2205 duplex stainless steel after two hours of electrochemical charging in different electrolyte volumes

# 3.4.2. Post-mortem SEM and EBSD analysis

Fractured specimens were investigated with SEM. Both the fracture surface and the normal surfaces were studied as illustrated in Figure 3-9 (a). Since hydrogen saturation was not aimed for in the present PhD, the fracture surfaces of hydrogen charged specimens always comprised of a hydrogen affected region near the edge and a hydrogen unaffected region in the centre, having a similar appearance as the fracture

surface of the corresponding reference specimen. A major advantage of this methodology is the possibility to evaluate the size of the zone with an altered fracture appearance and relate it to the hydrogen diffusion properties as well as the critical hydrogen concentration.

Apart from tensile testing until fracture, several tests were also stopped at an intermediate elongation. The chosen elongation depended on the studied material and the desired outcome. The interrupted specimens were also studied with SEM on the normal plane, see Figure 3-9 (b). Moreover, a large part of the dissertation focussed on the effect of hydrogen on the active deformation mechanisms in austenite. These mechanisms include dislocation-related processes but could also include deformation-induced twinning and deformation-induced martensitic phase transformation, both of which can be investigated by EBSD. Interrupted tensile specimens were chosen since the amount of deformation could be limited in comparison to fractured specimens. The higher the amount of deformation part of the macroscopic engineering stress-strain curve as the strain could not be determined locally in the necked region due to the restrictions when using an in-situ cell. Hydrogen-assisted cracking was analysed on both fractured and intermediately tensile tested specimens. Only surface cracks (in direct contact with the hydrogen atmosphere) were observed, i.e. on the normal surfaces indicated in Figure 3-9.



Figure 3-9: Schematic illustration of the investigated planes for fractured (a) and intermediate tensile test specimens (b)

Twin boundaries in austenite were predefined in the EBSD analysis software based on their orientation relationship as discussed in 3.2.2. The desired phases to be scanned for, must be added to the acquisition software before the start of a measurement. As the lattice of a'-martensite is only slightly tetragonal, data for BCC iron can be used for its indexation. No data for  $\varepsilon$ -martensite were, however, available in the software. The data were, therefore, created by adapting the Mg data with the correct lattice parameters. Mg was used for its predefined HCP crystal structure. The used lattice parameters for  $\varepsilon$ -martensite were a = 0.26 nm and c = 0.42 nm, which was chosen based on work performed by Verbeken et al. [182].

When error bars are presented on the experimental data, they represent the experimental standard deviation on the data points evaluated as only a partial sampling of the whole population. This standard deviation was added as ±1 sigma to the mean value.

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# Chapter 4 Critical evaluation of the hydrogen interaction with 2205 duplex stainless steel

# 4.1. Introduction<sup>1</sup>

Duplex stainless steels (DSS) are highly alloyed steels with a two-phase microstructure of ferrite and austenite. The first reference to DSS dates from 1927. Commercialization of the steel took place in the early '30s [183]. DSS were, however, only fully explored in the '70s since advanced steel making processes allowed for a better control of their microstructure [184]. The favourable combination of mechanical and corrosion properties fulfils the requirements of many industries such as chemical and petrochemical, oil and gas, marine transportation and pulp and paper industry [185, 186]. All these industrial applications are characterised by rather harsh environments where a significant strength level is required. For the oil and gas industry, DSS are for example used for subsea applications such as pipelines, valves and pumps [184]. In the chemical industry, they are e.g. used as high pressure pipes in urea plants [187].

DSS are typically alloyed with chromium, nickel and molybdenum and are classified in four different categories. The standard duplex stainless steels have a chromium content of about 22 wt%. Super duplex stainless steel have superior corrosion resistance due to a chromium content of approximately 25% and a molybdenum content of approximately 3%. In lean duplex stainless steels, the nickel and molybdenum content is reduced to lower the cost and compensated by a higher manganese and nitrogen content to guarantee the austenite/ferrite phase balance. Finally, hyper duplex stainless steels were developed for deep water offshore oil and gas applications which need extremely high pitting resistance achieved by a nitrogen content of up to 0.5 wt% [188].

Despite their growing usage worldwide, DSS components might fail during their lifetime when exposed to certain environments. DSS are in particular susceptible to hydrogen embrittlement. The generation of hydrogen in oil and gas industry can occur through the coupling of production tubing made out of DSS to carbon steel downhole casings [189]. Another possibility for hydrogen generation is impressed current cathodic protection, for instance for DSS pipelines in seawater. In sour environments, with pH lower than three, hydrogen can also be generated via localized corrosion [190].

<sup>&</sup>lt;sup>1</sup> The introduction of this chapter was based on the following two publications: L. Claeys, T. Depover, I. De Graeve and K. Verbeken, "Electrochemical hydrogen charging of duplex stainless steel", Corrosion 75-8 (2019), pp. 880-887, <u>https://doi.org/10.5006/2959</u> and L. Claeys, V. Cnockaert, T. Depover, I. De Graeve and K. Verbeken, "Critical assessment of the evaluation of thermal desorption spectroscopy data for duplex stainless steels: a combined experimental and numerical approach", Acta Materialia 186 (2020), pp. 190-198, <u>https://doi.org/10.1016/j.actamat.2019.12.055</u>

The two-phase austenite/ferrite microstructure of DSS complicates the study or prediction of the hydrogen embrittlement susceptibility due to the large discrepancies between both phases in terms of their interaction with hydrogen. Austenite is characterized by a high hydrogen solubility and a low hydrogen diffusivity, whereas ferrite shows a low hydrogen solubility and a high hydrogen diffusivity [191]. Moreover, duplex stainless steels are characterised by high internal stresses due to the largely different thermal expansion coefficient of both phases. These residual stresses are tensile in the austenite phase and compressive in the ferrite phase [192].

Multiple studies pointed out that the austenite fraction of a duplex stainless steel might be subjected to microstructural changes during hydrogen charging. Dabah et al. [193] demonstrated that hydrogen desorption induced surface tensile stresses provoking the phase transformation  $y \rightarrow \epsilon \rightarrow a'$  in duplex stainless steel. Martensitic phases induced by hydrogen charging and desorption were also observed by Glowacka et al. [194] and they correlated this transformation with the degradation of a theoretical FCC hydride phase created in austenite, which has an increased cell parameter because of hydrogen presence. Moreover, they also correlated it with the hydrogen-induced plastic strain. Glowacka et al. [195] also stated that the orientation relationship between austenite and ferrite grains might be important for a'martensite formation as favourably oriented ferrite grains can serve as nuclei for the transformation of austenite to a'-martensite. Yang et al. [196] stated that a critical current density exists at which a'martensite or *ɛ*-martensite formation takes place during cathodic hydrogen charging and subsequent outgassing of austenitic stainless steel. For every current density above this critical value, martensite formation took place after a certain charging time. This charging time decreased with increasing current density. The authors assumed that a'-martensite did not form during the charging procedure, but only after a certain outgassing time. However,  $\epsilon$ -martensite was observed immediately after charging. Apart from martensitic transformations, other microstructural changes were observed as well. Barnoush et al. [197] observed slip band formation on the surface of the austenite phase in a super DSS via atomic force microscopy during in-situ hydrogen charging. Observations were thus done on the level of individual grains. The phenomenon was explained by the nucleation and migration of dislocations. Luo et al. [198] combined electron backscatter diffraction (EBSD) and electron channeling contrast imaging (ECCI) and observed stacking fault formation in the austenite grains and an increase in dislocation density in ferrite after hydrogen charging of a DSS. Finally, Liang et al. [199] observed an increase in dislocation density of both austenite and ferrite in a super DSS after hydrogen charging. The dislocation density was determined via time-of-flight (TOF) neutron diffraction which provides information on bulk properties due to the large penetration depth of the used neutrons. When prestrain was applied to the DSS, the increase of the dislocation density in both ferrite and austenite due to hydrogen was rather limited.

Despite the complicated interaction of hydrogen with the microstructure during the charging procedure, DSS were charged with hydrogen in the past decade in order to evaluate their hydrogen embrittlement susceptibility. A large variety of environments was used to accomplish this. On the one hand, gaseous hydrogen charging at elevated temperature is possible. San Marchi et al. [200] used for example 138 MPa  $H_2$  gas at 573 K and charged 125 wppm in a 2507 DSS plate after 10 days. El-Yazgi et al. [201] used 22 MPa  $H_2$  gas at 623 K for 48 hours and charged 20 wppm in a 2205 DSS. On the other hand, electrochemical hydrogen charging with various electrolyte solutions is an option as well. Zakroczymski et al. [202] were able to charge 208 wppm in a 2.1 mm diameter UNS S31308 DSS bar using 0.1 M  $H_2SO_4$  with 10 mg/l  $As_2O_3$ as electrolyte and a current density of 20 mA/cm<sup>2</sup> for two weeks. Other electrolytes were also used by these the authors, but less hvdrogen was charged into the steel for the same charging time. The authors pursued a charging time that was assumed to result in saturation of both the ferrite and austenite phase fraction via diffusivity based calculations, but they did not confirm saturation experimentally. Dabah et al. [193] charged 156 wppm in a 0.6 mm SAF 2507 DSS plate using a 0.25 M  $H_2SO_4$  electrolyte solution with 0.25 q/L NaAsO<sub>2</sub> at 50 mA/cm<sup>2</sup> for 72 hours. Shorter charging times were tested as well. The hydrogen concentration still showed an increasing trend after 72 hours of charging meaning that saturation was not yet reached. Luo et al. [198] charged a 0.5 mm 2205 DSS plate in 0.5 M H₂SO₄ with 0.25 g/l As₂O₃ at 1.5 mA/cm<sup>2</sup>. The hydrogen evolution at a constant temperature of 50°C amounted to 8.5 wppm after two days of charging. Griffiths et al. [203] stated that hydrogen concentrations between 100 wppm and 250 wppm were needed in a 22% Cr duplex stainless steel to cause environment-assisted cracking after charging at 80°C in an acid brine environment. It is clear that a wide variety of hydrogen levels can be found in literature for hydrogen charged DSS depending among others on charging time, sample size, environment type, current density and hydrogen detection method. Saturation was never confirmed by means of experiments at different charging times. Moreover, in many studies, a homogeneous hydrogen concentration, despite being very relevant, was not aimed for to draw conclusions on the influence of hydrogen on various properties.

An important technique in the study of the hydrogen interaction with a DSS microstructure is thermal desorption spectroscopy (TDS). Few authors have published TDS measurements performed on duplex stainless steels so far. Yaqodzinskyy et al. [204] for example performed TDS on low alloyed 2101 duplex stainless steel and observed two peaks in their TDS spectrum. The authors stated that the first peak corresponded to lattice hydrogen and the second peak arose from hydrogen detrapped from dislocations. Dabah et al. [193] tested SAF 2507 DSS and found three peaks which they attributed to grain boundaries with an activation energy of 22.5-28.5 kJ/mol, dislocation cores with an activation energy of 34.8-40.3 kJ/mol and vacancies and/or austenite/ferrite interfaces with an energy of 50.2-57.4 kJ/mol. Silverstein et al. [205] performed TDS measurements on SAF 2205 DSS and observed four main peaks. The activation energies of the peaks were 24, 37, 44 and 62 kJ/mol, respectively. The authors mentioned various possible microstructural trapping features: elastic strain fields of dislocations (0-20 kJ/mol), screw dislocation cores or grain boundaries (20-30 kJ/mol), high angle grain boundaries, vacancies and austenite/ferrite interfaces (40-50 kJ/mol) and martensite (60 kJ/mol). The authors had extensive surface cracking due to the charging process which could have influenced the TDS spectra. It should be noted that all previous studies were performed on heterogeneously electrochemically hydrogen charged specimens where hydrogen did not reach the centre. This clearly affects the resulting desorption profile since hydrogen

effusion is controlled by a chemical potential difference throughout the material. Consequently, hydrogen can diffuse both towards the edge and the centre of the specimen.

In another study, Silverstein et al. [206] reported on TDS measurements performed on gaseous charged lean DSS, which contained a homogeneous hydrogen distribution after charging. The authors deconvoluted the signal into three peaks. While the first two peaks were attributed to hydrogen trapped at microstructural features, the third peak was ascribed to the sigma phase formed during gaseous hydrogen charging (67-72 kJ/mol). Park et al. [207] studied a DSS by gaseous hydrogen charging as well. The material was left in air for one day before testing. The resulting spectrum showed one broad peak. The authors concluded that hydrogen originated from austenite because of the similar appearance compared to TDS spectra of austenitic stainless steel. Further in-depth data analysis was however not provided. Consequently, no consensus has been reached so far on the shape of TDS spectra performed on duplex stainless steels nor on the analysis of possible hydrogen detrapping activation energies.

Recent literature focussed on the limitations of the Kissinger equation, especially in the case of diffusioncontrolled processes, as the possible delay by diffusion is neglected [75, 208]. This is very relevant for the present work since austenite is characterised by a low hydrogen diffusivity. Lattice diffusion in body centered cubic (BCC) iron occurs with an activation energy of approximately 8 kJ/mol [209]. Lattice defects such as dislocations, grain boundaries etc. have binding energies ranging from 20 kJ/mol to 60 kJ/mol [173, 210, 211, 212, 213]. Carefully designed carbides can reach higher binding energies [214, 215]. These features can thus be regarded as deep traps as compared to lattice diffusion in BCC steels and the detrapping activation energy can be determined reliably through the Kissinger equation. Lattice diffusion in face centered cubic (FCC) iron, however, has an activation energy of 51-55 kJ/mol. The binding energy between hydrogen and microstructural defects is similar to BCC iron, leading to the inability to characterise or evaluate them with TDS [74, 175]. This is also clear from experimental TDS data which showed that the application of cold work could be distinguished from TDS signals in the case of BCC steel while this was not the case for a fully FCC steel since an identical spectrum was obtained after cold work [216]. DSS combine both phases, i.e. ferrite and austenite, leading to difficulties in interpreting the TDS data with respect to hydrogen trapping. The derived approximate solutions of Fick's second law, which are controlled by both diffusion and (different types of) trapping published by Kirchheim [208], could provide important insights in hydrogen-microstructure interactions for this steel type.

The aim of the present work is to construct a charging curve for electrochemical hydrogen charging of UNS S32205 DSS and combine this with a study of the microstructural changes taking place due to the interaction of hydrogen with the microstructure. It also aims to perform TDS on electrochemically hydrogen charged DSS. The experimental study will be combined with numerical diffusion modelling based on the work of Kirchheim [208]. In the following subchapter, the microstructure of the studied DSS is first characterised.

Chapter 4

# 4.2. <u>Characterisation of the investigated duplex stainless steel</u>

The as-received duplex stainless steel was a hot rolled plate with a thickness of 0.8 mm. The chemical composition of the steel as provided by the manufacturer is given in Table 4-1. The alloy is designated as UNS S32205, more commonly known as 2205 duplex stainless steel.

Wt%	C	Cr	Ni	Мо	Mn	Si	Fe	Other
UNS S32205	0.022	22.85	5.5	3.07	1.81	0.32	Balance	Cu 0.2, P 0.027,
								Co 0.162, N 0.173

Table 4-1: Chemical composition of UNS S32205<sup>2</sup>

The chemical composition of a duplex stainless steel is chosen in such a way to obtain the wanted 50/50 phase balance. To accomplish this, various ferrite stabilising alloying elements on the one hand and austenite stabilising elements on the other hand were added. Chromium, molybdenum and silicon are ferrite stabilisers while nickel, manganese, carbon, nitrogen and copper are austenite stabilisers. For the analyses of the stable phases, a nickel and chromium equivalent is typically calculated [217].

Ni equivalent = (%Ni) + (%Co) + 30(%C) + 25(%N) +0.5(%Mn)+0.3(%Cu) = 11.61 wt% (4-1)

A Schaeffler diagram can be found in Figure 4-1. The composition of the 2205 DSS used in the present study was added to the graph in red. Figure 4-2 shows the thermodynamical equilibrium phase fractions as a function of the temperature as calculated with Thermocalc for the exact composition of the studied 2205 DSS. The temperature for hot rolling and subsequent quenching should be around 1120°C in order to have an equal phase balance required for the optimum combination of properties.

Partitioning of the alloying elements into the different phases typically takes place. The partitioning is a function of temperature, i.e. quenching at a different temperature would have resulting in a different amount of the alloying elements in the two phases [218]. An EDX analysis is shown in Figure 4-3. The ferrite stabilising elements, i.e. chromium, silicon and molybdenum, showed an increased fraction in the ferrite phase while the austenite stabilising elements, i.e. nickel and manganese were enriched in the austenite phase. Elements such as carbon or nitrogen cannot be determined accurately with EDX and are therefore not presented in the graph.

The phase fractions of the studied DSS were evaluated with a Feritscope. A Feritscope is a device able to measure phase fractions based on differences in magnetic properties. Depending on its crystal structure, steel can either be ferromagnetic (BCC or BCT) or paramagnetic (FCC). The device is able to separate accurately the ferromagnetic phases from the paramagnetic phases in a representative volume of the

<sup>&</sup>lt;sup>2</sup> Aperam Genk is acknowledged for the received material.

material. This is especially interesting for the present work since ferrite (BCC) and austenite (FCC) have different magnetic properties and can as such be distinguished with a Feritscope. The austenite fraction of the as-received 2205 DSS was determined to be 53±2% based on ten measurements.



Figure 4-1: Schaeffler diagram showing stable phases after heating to 1050°C for 30 minutes and quenching in water ( [217] adapted from [219]), the composition of the UNS S32205 DSS is indicated in red



Figure 4-2: Phase fraction (mole) as a function of temperature calculated with Thermocalc with the composition of 2205 DSS as shown in Table 4-1



Figure 4-3: Partitioning of the different alloying elements in the two phases of the DSS

Duplex stainless steels have a very specific microstructure due to their production process. The production starts by casting the alloy into a slab. The as-cast microstructure consists of three different zones depending on the distance from the surface. The cooled surface shows fine equiaxed grains, followed by a columnar zone and coarse equiaxed grains in the centre. The microstructure consists of a delta ferrite matrix with austenite inclusions [220]. The slab is subsequently reheated and hot rolled to a plate. With increasing rolling reduction, the as-cast microstructure evolves to a more and more elongated structure along the rolling direction. The steel is eventually quenched from a temperature where the desired phase balance is present for the given chemical composition. Fast cooling ensures that the phase balance is maintained at room temperature. When the quenching step is not done carefully, harmful intermetallic phases can be formed, e.g. sigma phase, which can deteriorate the mechanical properties [220, 221]. The cooling rate that should be reached is a function of the alloying elements.

Optical microscopy was performed on the 2205 DSS studied in this research to reveal its complex microstructure. Figure 4-4 schematically shows the three main planes that can be defined after the hot rolling process and their corresponding optical microscopy images. Etching was performed with Beraha II etchant (HCl, H<sub>2</sub>O, F<sub>2</sub>H<sub>5</sub>N and K<sub>2</sub>SO<sub>5</sub>) which clearly accentuated the two different phases (light phase = austenite). The TD plane (A) consists of alternating layers of austenite and ferrite. The RD plane (B) shows the same oriented structure, however, the austenite grains are less prolonged. The ND plane (C) shows large areas consisting of the same phase. The main phase fraction observed in images of the ND plane depends largely on the location of the section with respect to the layered microstructure. The ferrite phase is interconnected through the thickness. The austenite phase was mainly present as separate islands with some interconnection over the thickness as well. A small segregation zone was present in the centre of the specimen. Here, the highest possibility for the formation of sigma phase is present, which is an intrinsically brittle phase that deteriorates the mechanical properties when present in too large quantities. It is typically formed when the cooling rate is not high enough, e.g. in the centre of the rolled steel plate.

Manufacturers try to maintain a value below 1% which should not deteriorate the mechanical properties too much. In the present steel, this was successfully executed.



Figure 4-4: Optical microscopy images of different planes in 2205 DSS, light phase = austenite, dark phase = ferrite, A = RDxND plane, B = TDxND plane, C = RDxTD plane

An SE image of the etched microstructure of the 2205 DSS on the TD plane is shown in Figure 4-5. The ferrite and austenite phases are clearly distinguishable by their different topological appearance after etching. To have a further in-depth characterisation of the microstructure, EBSD was performed. Figure 4-6 shows EBSD measurements performed on the ND plane (a,b) and on the TD plane (c,d) including image quality maps and phase maps. High angle grain boundaries were indicated in black on the phase maps. The ferrite grains within the layers were very prolonged and showed not many grain boundaries in the presented image of the TD plane. The austenite grains were clearly smaller. Annealing twin boundaries were observed in the austenite phase (straight and mostly two parallel lines). From various EBSD scans it was concluded that the layers had an average thickness of  $1.49 \pm 0.1 \,\mu\text{m}$ .

# Chapter 4



Figure 4-5: SE image of TD plane 2205 DSS etched with Carpenter's etchant



Figure 4-6: EBSD characterisation of the microstructure of as-received 2205 DSS (a) IQ map and (b) phase map of ND plane, (c) IQ map and (d) phase map of TD plane

# 4.3. <u>Electrochemical hydrogen charging of duplex stainless steel</u><sup>3</sup>

Electrochemical hydrogen charging has proven to be an efficient method to charge BCC steels with a homogenous hydrogen concentration. Hydrogen charging of duplex stainless steels is however more challenging due to the lower global hydrogen diffusion coefficient because of the presence of approximately 50 vol% of austenite, which has an inherent lower hydrogen diffusion coefficient compared to BCC phases. Electrochemical hydrogen charging was performed at a constant current density of 0.8 mA/cm<sup>2</sup> in an 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution containing 1 g/L thiourea. Prior to hydrogen charging, the surface oxide layer was removed by grinding. Metal oxides, including those of steel, are stated to have an inhibiting effect on hydrogen absorption reducing the hydrogen permeability with at least one order of magnitude [222]. The as-received plate thickness was reduced to 0.3 mm with an accuracy of ± 10 µm by mechanical grinding in order to reach a homogeneous hydrogen concentration in a reasonable amount of time. The side surfaces were finished with #320 grinding paper. The total hydrogen concentration charged into the DSS plate was determined after different applied charging times with melt extraction. Three tests were performed for every applied charging time to obtain confirmation of the obtained values. Figure 4-7 shows the results of the melt extraction tests at different charging times.



**Figure 4-7: Total hydrogen concentration as a function of charging time as measured with melt extraction** A theoretical saturation curve was constructed by solving Fick's second law (4-3) for one dimensional diffusion [223]:

<sup>&</sup>lt;sup>3</sup> This subchapter was based on the following publication: L. Claeys, T. Depover, I. De Graeve and K. Verbeken, "Electrochemical hydrogen charging of duplex stainless steel", Corrosion 75-8 (2019), pp. 880-887, <u>https://doi.org/10.5006/2959</u>

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$
(4-3)

where C(x,t) is the hydrogen concentration [wppm], x [m] the position, t [s] the time for diffusion and D  $[m^2/s]$  the hydrogen diffusion coefficient. The initial condition (t=0) was a zero hydrogen concentration at every position. Appropriate boundary conditions were chosen by assuming a sheet of thickness 2l with a symmetric concentration profile (4-4) and by maintaining both surfaces of the sheet at a constant concentration C<sub>0</sub> during the hydrogen charging procedure (4-5). The latter assumes that the potential remained constant during charging which was also observed during the course of the experiment. The sheet was symmetric about x=0 occupying the region  $-l \le x \le l$ .

$$\frac{\partial C}{\partial x} = 0, \ x = 0, \ t \ge 0$$
(4-4)

$$C = C_0, x = l; -l, t \ge 0$$
 (4-5)

Solving the one dimensional diffusion equation with these boundary conditions resulted in a timedependent expression for the hydrogen concentration profile through the thickness of the material (4-6) [223].

$$\frac{C}{C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot \exp\left(-\frac{(2n+1)^2 \cdot \pi^2 \cdot D \cdot t}{4l^2}\right) \cdot \cos\left(\frac{(2n+1) \cdot \pi \cdot x}{2l}\right)$$
(4-6)

The total hydrogen concentration as a function of charging time was subsequently calculated by integrating the concentration profile over the given sample thickness and dividing it by 2l. The final equation is given in equation (4-7) where the value of  $C_0$  is replaced by  $C_{s_1}$  i.e. the equilibrium surface hydrogen concentration [wppm], as this is the maximum concentration that can be reached in the steel.

$$C_{\rm H}(t) = C_{\rm S} \cdot \left(1 - \frac{4}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \cdot \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4l^2}\right) \cdot \left(\sin\left(\frac{(2n+1)\pi}{2}\right) - \sin\left(-\frac{(2n+1)\pi}{2}\right)\right)$$
(4-7)

A fit of the analytical solution of Fick's second law was obtained by minimizing the quadratic difference between experiment and solution with respect to D and C<sub>s</sub>. The value of C<sub>s</sub> was initialised based on the experimental data. The value of D was initialised based on literature as 2.2E-14 m<sup>2</sup>/s. Reported values in literature for the hydrogen diffusion coefficient of 2205 duplex stainless steel range from 2.2E-14 m<sup>2</sup>/s to 6.4E-14 m<sup>2</sup>/s [72, 224, 225, 226]. The result is shown in Figure 4-8. The equilibrium surface concentration C<sub>s</sub> amounted to 710 wppm. The hydrogen diffusion coefficient D was determined to be 9.6E-15 m<sup>2</sup>/s.



diffusion law

From the results presented in Figure 4-8, it is clear that several weeks of electrochemical hydrogen charging in a sulphuric acid solution containing thiourea were required to reach saturation. After 21 days of hydrogen charging, saturation was not fully reached yet. The fitted model based on Fick's second law for diffusion resulted in a diffusion coefficient of 9.6E-15 m²/s. This diffusion coefficient should be interpreted as an effective diffusion coefficient for the overall duplex stainless steel. The variation on literature data including this value can be linked to differences in grain size, austenite phase fraction and the relation between the hydrogen diffusion direction and the elongated grain direction in the DSS microstructure. Hydrogen diffusion will, for instance, be faster when it is parallel to the elongated grain structure [32]. Hydrogen diffusion in the present case was perpendicular to the elongated grains. A value at the lower end of the range could thus be expected. Apart from the effective diffusion coefficient, a hydrogen concentration at saturation of 710 wppm was found from the model fit. This hydrogen concentration is one to two orders of magnitude higher than typical values for BCC steels [213, 227]. Reported literature data on hydrogen concentrations for DSS are in the same order of magnitude although no values as high as 700 wppm were mentioned. However, saturation was never confirmed in literature. The theoretical equation for hydrogen diffusion (4-5) and an effective diffusion coefficient based on literature, i.e. 2.2E-14 m<sup>2</sup>/s, were therefore used to estimate saturation concentrations based on hydrogen concentrations found in literature for electrochemical hydrogen charging tests in similar electrolytes that were not continued until saturation. Dabah et al. [193] charged 156 wppm in a 0.6 mm plate after 72 hours of charging. According to our theoretical model, 24.4% of the saturation concentration was reached with these parameters. The saturation concentration then amounts to 639 wppm which is slightly lower than the value found in this work. The DSS was, however, heated to 450°C to determine the hydrogen concentration while in the present work, melt extraction was performed as such potentially releasing more hydrogen. Zakroczymski et al. [202] detected 208 wppm in a 2.1 mm diameter DSS cylinder after two weeks of hydrogen charging. Considering the diffusion equation in cylindrical coordinates (4-8), the mean concentration in the cylinder similar to equation (4-7) for a plate material can be calculated (4-9) [228]. With the parameters used, 32.7% of the saturation concentration was obtained according to the calculation. Saturation would then amount to 637 wppm.

$$\frac{\partial C}{\partial t} = D \cdot \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r}\right)$$
(4-8)

$$C_{H}(t) = C_{S} \cdot (1 - \frac{4}{R^{2}} \sum_{n=1}^{\infty} \frac{1}{\beta_{n}^{2}} \cdot \exp(-D \cdot \beta_{n}^{2} \cdot t))$$
(4-9)

with 
$$\beta_1 = \frac{2.405}{R}$$
;  $\beta_2 = \frac{5.520}{R}$ ;  $\beta_3 = \frac{8.654}{R}$ ;  $\beta_4 = \frac{11.7915}{R}$ ; R = radius [m]

In duplex stainless steels, it can be assumed that hydrogen diffusion occurs mainly through the ferrite phase. Ferrite is a so-called highway for hydrogen transport. Turnbull et al. [229] stated that the overall contribution of austenite to the diffusion flux in a duplex stainless steel is negligible in hydrogen permeation tests, despite the higher hydrogen solubility. Mente et al. [230] constructed a FE model for hydrogen diffusion in DSS taking into account the two-phase microstructure and found that ferrite was charged quickly followed by slow charging of the austenite phase. Ferritic stainless steels with compositions close to the composition of the present ferrite phase fraction, are typically saturated in a time frame of hours, e.g. approximately three hours were needed to saturate a 1 mm thick ferritic stainless steel plate which resulted in a fitted diffusion coefficient of 4.3E-11 m²/s [231]. Owczarek et al. [232] calculated values for the diffusion coefficient of ferrite and austenite separately in a DSS and found 1.5E-11 m<sup>2</sup>/s for ferrite and 1.4E-16 m<sup>2</sup>/s for austenite. A fully ferritic plate of 0.3 mm would then take approximately one hour to saturate while a fully austenitic plate would need about ten years to saturate (99% filled). However, as hydrogen is transported to all austenitic grains in the specimen thickness through the percolated ferrite phase, the austenite grains can be considered as thin plates with a thickness of 1.5 μm to which equation (4-5) can be applied. An austenite grain then needs 2 hours to be saturated with hydrogen (99% filled) assuming hydrogen is charged from both sides. The total charging time of the present duplex stainless steel should therefore be in the order of hours. However, several days were needed (cf. Figure 4-7). Several factors might decelerate the diffusion process of hydrogen in ferrite of duplex stainless steels. Turnbull et al. [229] stated that hydrogen diffusion in duplex stainless steels at moderate temperatures is dominated by trapping at the austenite/ferrite interface. These trapping events decelerate the permeation rate through the ferrite phase. Moreover, hydrogen has to surround the austenite islands. This results in longer effective diffusion paths. Owczarek et al. [232] used a tortuosity factor to describe the deceleration of hydrogen diffusion by the austenite phase and found values of approximately 2 to 6 for a DSS with a membrane thickness of 0.3 mm, a grain size of 12  $\mu$ m, 40 vol% of austenite and hydrogen diffusion parallel to the elongated grains. In the present case, an even more

significant deceleration is expected as the DSS contains a higher austenite phase fraction and considerable smaller grain size. Moreover, hydrogen diffusion occurred perpendicular to the elongated grains.

It should be noted that the two-phase nature of DSS implies the presence of variations in surface condition as the native oxide film on DSS is different for the ferrite and austenite phase. The native oxide on a (001) ferrite grain was, for example, found to contain more Cr<sub>2</sub>O<sub>3</sub> than the (001) austenite grain [233]. This could influence the local hydrogen adsorption/absorption properties. Local electrochemical techniques should be able to characterise differences in hydrogen absorption. The long charging time under reducing conditions and the bulk hydrogen detection method used in the present work make it, however, impossible to observe differences related to the oxide film.

An in-depth investigation was performed on the hydrogen/material interaction during charging as many authors observed microstructural changes due to the presence of hydrogen [194, 196, 197, 198]. The microstructural changes as a consequence of hydrogen charging were evaluated for different charging times. After eighteen hours of hydrogen charging, a clear surface relief in the austenite phase was observed, as shown in Figure 4-9, whereas no noticeable changes were seen in the ferrite phase. The microstructural evolution after 7 days of hydrogen charging was evaluated as well. Similar to the results after eighteen hours of hydrogen charging, a surface relief was observed for the austenite phase. EBSD was used to study the presence of both hydrogen-induced a'-martensite and hydrogen-induced  $\varepsilon$ -martensite. Three different phases were considered as possible in the EBSD software, i.e. y-iron, a-iron and  $\varepsilon$ -martensite. As a'-martensite is very similar to a-iron, this phase was not loaded separately. In order to obtain high quality EBSD results, the surface was slightly re-polished after charging, which removed the surface relief. An ND IPF map and phase map of both the surface and cross-section of the charged specimen were made, as shown in Figure 4-10 and Figure 4-11, respectively. No indications of martensite phases were observed inside austenite grains in any of the performed measurements. The inverse pole figure of the hexagonal  $\varepsilon$ -martensite phase was therefore not added to the figures.

Since no martensitic phase transformations were observed, most likely the charging procedure was not severe enough to initiate phase transformations as other authors used higher current densities during electrochemical hydrogen charging. Nevertheless, the surface study revealed that other microstructural changes took place in the austenite phase during the first hours of hydrogen charging. Surface relief, consisting of various parallel lines with a certain spacing, was observed. The lines did not penetrate grain or phase boundaries. In some grains, parallel lines were formed in more than one direction. Similar features were observed during plastic deformation of duplex stainless steel [234, 235], indicating that the phenomenon taking place can be linked to plastic deformation of the austenitic phase. Most likely, the surface relief can be attributed to the presence of slip bands arising from dislocation movement towards the surface. The surface relief was easily removed by a short polishing procedure. Typical slip band heights are about 20-30 Burger vectors [236], which is consistent with the easy removal by polishing.

Barnoush et al. [197] observed comparable surface changes with optical microscopy and atomic force microscopy during in-situ electrochemical charging of super duplex stainless steel. These authors stated that a high enough hydrogen concentration reduces the shear modulus. Teus et al. [166] also reported that hydrogen reduced the shear modulus based on their density functional theory (DFT) calculations. Due to the lowered shear modulus, Frank-Read sources start producing new dislocations under the high internal stress inherent to duplex stainless steels. Duplex stainless steels are indeed quenched from verv high temperatures at which the phase balance is ideal. The large difference in thermal expansion coefficient between the two phases results in high tensile stresses in the austenite phase and high compressive stresses in the ferrite phase [237]. Consequently, newly emerged and already existing dislocations start migrating and the ones reaching the surface produce the surface relief known as slip bands. Luo et al. [198] observed similar features in the austenite phase by combining EBSD and ECCI analyses of DSS samples exposed to hydrogen charging and concluded that the lines were caused by dislocations that developed into stacking faults rather than into slip bands. Other proof for dislocation nucleation during hydrogen charging of duplex stainless steels has been given by Liang et al. [199], who measured the dislocation density of a super duplex stainless steel with time-of-flight (TOF) neutron diffraction. They observed an increase in dislocation density with one order of magnitude in austenite after hydrogen charging. It should also be noted that dislocation movement can be facilitated in the presence of hydrogen as proposed by the hydrogen enhanced localized plasticity (HELP) model [213, 113]. Dislocation nucleation and migration is, however, not a continuous event over the charging procedure. The dislocation density typically reaches a saturation level because dislocation movement is hindered by obstacles such as other dislocations. Moreover, the available stress level is limited as there is no externally applied stress and dislocation movement results in stress relief. In-situ measurements showed indeed that the evolution of slip lines seemed to stop or slow down [197]. It should be noted that the dislocation density might also have increased in the ferrite phase due to hydrogen charging as there are high internal stresses in the ferrite phase as well. Liang et al. [199] indeed observed an increase in the dislocation density in the ferrite of a super DSS with neutron diffraction. The increase was, however, not as large as in the austenite phase. Luo et al. [238] observed enhanced dislocation movement and dislocation multiplication in the ferrite phase fraction of 2205 DSS due to absorbed hydrogen as well. Fréchard et al. [234] performed tensile tests on DSS and mentioned that austenite showed multiple slip bands while ferrite showed no slip bands in the beginning and a limited amount of slip bands close to the austenite phase boundary at higher strain levels. Two distinct reasons can therefore be considered for the absence of slip lines in the ferrite grains in our samples. First, the stress level was possibly insufficient for slip band formation in ferrite. Secondly, the observed lines in the austenite grains are stacking faults. Dislocations do not develop into stacking faults in ferrite due to the higher stacking fault energy.

The overall increase in the dislocation density in both the austenite and ferrite phase due to hydrogen charging resulted most likely in a higher hydrogen concentration compared to the initial state as dislocations attract hydrogen and thus increase the hydrogen solubility of a material, however, in the

austenitic phase, the increase in the hydrogen concentration due to trapping sides provided by cold work was not very large [239]. The increase in dislocation density cannot be avoided as the high internal stresses, providing the necessary stress level for dislocation nucleation, are inherent to the production process of duplex stainless steels. The applied experimental methodology in this work can, therefore, be considered as a reliable procedure to saturate duplex stainless steels with hydrogen as no damage in the form of cracks or martensite formation was observed which would affect hydrogen diffusion and hydrogen trapping to a much larger extent.



Figure 4-9: Microstructural surface changes after 18 hours of electrochemical H charging of DSS: formation of slip bands in austenite



Figure 4-10: ND plane microstructure of DSS after 7 d of hydrogen charging and re-polishing: (a) SE image, (b) ND IPF map, and (c) phase map



Figure 4-11: TD plane microstructure of DSS after 7 days of hydrogen charging (a) SE image, (b) ND IPF map and (c) phase map

# 4.4. <u>Critical evaluation of thermal desorption spectroscopy data for duplex stainless steel: a combined</u> <u>experimental and numerical approach</u><sup>4</sup>

Thermal desorption spectroscopy tests were performed on 0.3 mm thick specimens obtained by grinding the material. The side surfaces were finished with #320 grinding paper. Two different charging times were applied, i.e. one day and fifteen days of charging. The applied heating rate determines to a large extent the position of the peaks. Two heating rates frequently applied to study BCC steels were also applied on the present duplex stainless steel, i.e. 600 K/h and 900 K/h [208, 173, 211, 212]. Following the suggestion of Kirchheim [208] stating that diffusion and trapping can be separated more easily when slow heating rates are applied, 20 K/h, 35 K/h and 50 K/h were additionally used.

Figure 4-12 shows the experimentally obtained TDS data. The results of the fast heating rates (600 and 900 K/h can be found in Figure 4-12 (a), while the slow heating rate results (20, 35 and 50 K/h can be found in Figure 4-12 (b). The maximum flux decreased with decreasing heating rate which is expected to be due to the longer test time [208]. The spectra of the specimens charged for 15 days showed a different shape depending on the applied heating rate. The fast heating rates (Figure 4-12 (a), 15d H) resulted in one asymmetric peak with a rather flat top. The slow heating rates (Figure 4-12 (b), 15d H) resulted in a small peak followed by a two-step peak. The specimens charged for one day (1d H) showed one main peak followed by a shoulder finishing at approximately the same temperature as the corresponding fifteen days charged specimen tested at 50 K/h showed an additional small peak in the beginning as was also the case for the fifteen days charged specimens at this heating rate (cf. Figure 4-12 (b)).

Two models were constructed in order to simulate the experimental thermal desorption spectra. Hydrogen diffusion according to Fick's law was implemented in these models, however, trapping was not included. The first model assumed that the material was homogeneous with one global, temperature dependant, hydrogen diffusion coefficient and an average hydrogen solubility. The average solubility can be understood as the sum of the solubilities in ferrite and austenite weighted by their phase fraction in the duplex steel. The second model considered the heterogeneous structure of duplex stainless steel (cf. 4.2). The material was modelled as a combination of two phases, each with their own hydrogen diffusion coefficient and solubility. On the interface of both phases, local equilibrium was assumed with consideration of a partitioning constant. By comparing both models to the experimental data, insight in the contribution of hydrogen diffusion to TDS curves was obtained. As such, the potential impact of hydrogen trapping on the experimental TDS curves can be evaluated as well.

<sup>&</sup>lt;sup>4</sup> This subchapter was based on the following publication: L. Claeys, V. Cnockaert, T. Depover, I. De Graeve and K. Verbeken, "Critical assessment of the evaluation of thermal desorption spectroscopy data for duplex stainless steels: a combined experimental and numerical approach", Acta Materialia 186 (2020), pp. 190-198, <u>https://doi.org/10.1016/i.actamat.2019.12.055</u>



Figure 4-12: Experimental TDS data of 2205 DSS for different charging times (1 day and 15 days) and heating rates (a) fast heating rates (600 and 900 K/h) and (b) slow heating rates (20, 35 and 50 K/h)

Homogeneous hydrogen diffusion was simulated using Fick's second law in its one-dimensional form, presented now with a clear time/temperature dependency (4-10) [208, 223]:

$$\frac{\partial C}{\partial t}(x,t) = D(T(t))\frac{\partial^2 C}{\partial x^2}(x,t)$$
(4-10)

With C(x,t) the time (t) - and position (x) -dependent hydrogen concentration [wppm], D the temperaturedependent hydrogen diffusion coefficient [m<sup>2</sup>/s], T the temperature [K], t the time [s] and x the position [m]. The diffusion coefficient is thus also dependent on the time since temperature and time can be linked through the constant heating rate (HR [K/h]), i.e. T(t) = HR\*t.

Both the charging and discharging procedure were modelled to reproduce the experimentally obtained TDS signals. For charging, the initial concentration profile (t=0) was zero throughout the thickness of the specimen. The temperature was kept constant. The boundary condition (4-11) for the simulation of hydrogen charging was:

$$C(0,t) = C(d,t) = C_S t > 0$$
(4-11)

With d the thickness of the plate [m] and C<sub>s</sub> the equilibrium surface concentration for the given experimental parameters [wppm]. Constant concentration boundary conditions were chosen since the potential did not vary significantly during the prolonged charging time. The differential equations were evaluated numerically with Forward-Time-Central-Space (FTCS) finite differentiation. The spatial discretion was 6 µm. The time discretization was chosen based on the Von Neumann stability criterion, i.e.

 $0.2 * \frac{(\frac{1}{2}dx^2)}{\max(D(t))}$  with a maximal value of one second, in order to ensure an accurate and stable simulation. Different charging times were simulated including the experimentally used charging times. For discharging, the concentration profile at the end of charging was used as initial condition. The boundary condition (4-12) for discharging was:

$$C(0,t) = C(d,t) = 0 \ t > 0$$
(4-12)

The spatial and time discretion were identical to the case of charging. To eventually obtain a signal that can be compared with experimental TDS curves, the flux J [wppm/s] (4-13) was determined in the following way:

$$J(t) = -\frac{\partial \bar{c}(t)}{\partial t}$$
(4-13)

In this equation,  $\overline{C}$  is the time-dependent average concentration [wppm].

As discharging deals with increasing temperatures, the relationship between diffusion coefficient and temperature should be known. Turnbull et al. [240] reported  $D_{eff}(t) = 2.8E-8 \exp\left(-\frac{39300}{RT(t)}\right) m^2/s$  for 2205 duplex stainless steel. The hydrogen saturation level was taken equal to 710 wppm, based on the fit of the melt extraction data as illustrated in Figure 4-8. These data were used in the initial simulations.

To verify whether duplex stainless steels can be treated as a homogeneous material with an average hydrogen diffusion coefficient and concentration, a model considering the two-phase microstructure of the material was used as well. The microstructure of the DSS was modelled by using a 2D phase field f which describes the distribution of ferrite (f=0) and austenite (f=1) inside the material. An example of the modelled phase distribution is indicated in Figure 4-13. Symmetry conditions were applied to halve the calculation time. The grain size was 2.5 times larger than the studied material to further limit calculation time since the simulation time scales with  $\left(\frac{1}{dw}\right)^4$ . An adequate volume fraction of the phases was created to remain close enough to the actual material, i.e. 53% of austenite. The austenite and ferrite phase were characterized by quite different hydrogen diffusion coefficients and solubilities. The temperature dependent diffusion coefficients for both ferrite and austenite were taken from literature. The effective diffusion coefficient for ferritic stainless steel type AL 29-4-2 was  $D_{eff}(t) = 8.45E-6 \exp\left(-\frac{33700}{RT(t)}\right) m^2/s$ [216]. This value includes the delay caused by trapping at microstructural features and substitutional atoms. The diffusion coefficient for austenitic stainless steels (average of six different alloying compositions) was  $D_{eff}(t) = 5.76E-7 \exp\left(-\frac{53620}{RT(t)}\right) m^2/s$  [74]. The solubility difference was introduced by a partitioning coefficient on the cell faces between the two phases. For the sake of simplicity, a value of 10 wppm was chosen for the ferrite solubility since literature reports on the solubility of hydrogen in ferritic stainless steels range from 5 to 40 wppm [241, 242, 243, 244]. The partitioning coefficient was subsequently determined based on the equilibrium surface concentration and the known phase fractions.



Figure 4-13: Duplex microstructure model for TDS diffusion simulation. Absorption or desorption is possible from the top surface (white = ferrite, black = austenite)

Again, both hydrogen charging and discharging were simulated. For charging, the initial concentration was zero throughout the material. The boundary condition during charging consisted of a constant surface concentration of 10 wppm, i.e. the ferrite solubility chosen from literature data. The microstructure was also designed is such a way that only ferrite was present at the surface for calculation stability reasons. Since the diffusion coefficient depends on the position as well as the time in the present model, Fick's second law was no longer used as starting equation. Instead, a finite element method was used with square elements with a spatial discretion dx of 8.65E-7 m. The hydrogen flux was evaluated over every edge in the x- and y-direction following Fick's first law for diffusion. When a phase boundary is reached, the lower value for the diffusion coefficient is used, i.e. the value of austenite. To account for uphill diffusion, the partitioning coefficient served as scaling factor for the criterion leading to a hydrogen flux. The concentration change in an element is evaluated as the difference of the outgoing and incoming flux. For discharging, the initial condition was the 2D concentration as simulated by the charging procedure. The surface concentration was put to zero. The outgoing flux at the surface side was used to calculate the signal as observed during TDS tests. The numerical approach was the same as for charging. In all simulations, time discretization was chosen  $0.2*rac{(rac{1}{2}dx^2)}{D_f}$  with a maximal value of ten seconds in order to reach convergence. The diffusion coefficient of the ferrite matrix was used to have the most strict condition, i.e. this implies a smaller time step.

In order to be able to analyse the experimental data, the model based on homogeneous hydrogen diffusion with a value for the hydrogen diffusion coefficient reported by Turnbull et al. [229] was first used to simulate TDS spectra. Several charging times were modelled including the two experimentally tested charging times (1 and 15 days). Figure 4-14 shows the simulated hydrogen concentration profiles through the thickness after charging. 150 days of charging would result in a homogeneously charged material. The other simulated charging times had a significantly lower hydrogen concentration in the centre of the material.

Figure 4-15 shows the corresponding numerical thermal desorption curves at two different applied heating rates, i.e. 900 K/h and 50 K/h. Both a fast and a slow heating rate were thus simulated. The shape of the TDS spectra differed strongly for different charging times. Short charging times (1 and 5 days) resulted in one main peak followed by a shoulder. Longer charging times (15 and 30 days), where hydrogen reached the centre of the specimen (cf. Figure 4-12), resulted in a two-step peak. Charging times approaching a homogeneous hydrogen concentration (50 and 150 days) gave rise to one main asymmetrical peak. Similar shapes were experimentally observed in literature when DSSs were homogeneously charged via gaseous charging [206, 207]. The first peak shifts to higher temperatures with increasing charging times as indicated by the vertical line on both figures. The two simulated heating rates resulted in similar peak shapes for corresponding charging times.



Figure 4-14: Simulated hydrogen concentration profile through the thickness for different charging times (homogeneous diffusion coefficient from [240])



Figure 4-15: Simulated TDS data for different charging times and different heating rates: (a) 900 K/h and (b) 50 K/h (homogeneous diffusion coefficient from [240], the vertical lines indicate a common peak for all charging times)

The diffusion activation energy (4-14) can be determined with the following equation:

$$\frac{\partial (\ln \left(\frac{\theta}{T_{m}^{2}}\right))}{\partial (\frac{1}{T_{m}})} = -\frac{Q}{R}$$
(4-14)

With 0 the heating rate [K/s], T<sub>m</sub> the maximal peak temperature [K], Q the diffusion activation energy [J/mol] and R the universal gas constant [J/K/mol]. The validity of the model was checked by determining the diffusion activation energy from both the first and second peak. Based on the peak positions of the common second peak (cf. vertical lines in Figure 4-15), the imposed energy value of 39.3 kJ/mol [240] was obtained. Additionally, analysis of the positions of the first peaks resulted in the same imposed energy value. It is important when analysing the first peak that equal charging times are compared since the position is influenced by the charging time. It can thus be concluded that both the first and second peak, arising from the same diffusion process, are all characterized by the same diffusion activation energy.

The experimental data were analysed in a similar way as the numerical data, since the shape of the curves showed a lot of correspondence. Firstly, the diffusion activation energy was calculated based on the common second peaks in Figure 4-12. Additionally, the first peak was used for one day and fifteen days of charging separately. Only the curves with clearly distinguishable peaks were used. The temperature at which the slope of the experimental curve changed for the fifteen days charged specimens was chosen as peak maximum (only distinguishable for 50, 35 and 20 K/h). The result can be found in Figure 4-16. This procedure resulted in an average activation energy of  $43.4 \pm 1.5$  kJ/mol which can be interpreted as the effective diffusion activation energy of this material.



Figure 4-16: Diffusion activation energy determined from experimental TDS curves of 2205 DSS via the Kissinger equation

The average experimentally obtained diffusion activation energy, i.e. 43.4 kJ/mol, was implemented in the model. The pre-exponential factor was determined through visual correspondence with the experimental TDS data. This resulted in an equation for the effective hydrogen diffusion coefficient:  $D_{eff} = 3E-7*exp(-\frac{43400}{RT}) m^2/s$  which is in good agreement with the equation reported by Turnbull et al. [240]. Figure 4-17 shows the obtained fits with the experimental data as shown in Figure 4-12, based on this  $D_{eff}$ .



Figure 4-17: Fit of the homogeneous diffusion model to the experimental TDS data (a) fast heating rates (600 and 900 K/h) and (b) slow heating rates (20, 35 and 50 K/h) (experimentally obtained  $D_{eff} = 3E-7*exp(-\frac{43400}{RT}) m^2/s)$ 

In the case of heterogeneous hydrogen charging, two peaks were thus observed, both experimentally and via simulation. This can be explained as follows: hydrogen can go two ways, either directly to the surface (first peak) or to the uncharged centre and then finally to the surface (second peak). The two peaks can thus be linked to different paths towards the surface, a short one and a long one. The position of the first peak depends on the depth of charging while the position of the second peak depends on the specimen thickness, which was kept constant during the experiments. The depth of charging time until it equals the specimen thickness. The diffusion activation energy can therefore also be evaluated by a modified Kissinger analysis of the first peak position determined at different charging times. As illustrated in [208], this analysis leads to a modified Kissinger plot of ln(l²/T) versus 1/T, with l [m] the depth of charging and T[K] the maximum peak temperature.

Pu et al. [245] also modelled TDS spectra obtained on 304 austenitic stainless steel including trapping and concluded that the high temperature tail could indeed not be explained by trapping. Similarly, Yagodzinskyy et al. [175] analysed TDS spectra of heterogeneously charged austenitic stainless steels using an analytical solution of Fick's law. The authors also concluded that diffusion of hydrogen which comes

from the opposite surface layer was responsible for the high temperature tail. Additionally, the second peak did not differ in position for different charging times. Consequently, part of the hydrogen atoms always followed the longest possible diffusion path. When a sufficient amount of hydrogen is present in the centre of the specimen after charging (cf. 50 and 150 days charging in Figure 4-15), the subdivision into two peaks did no longer occur.

As stated, the overall shape of the TDS curves is very well fitted by the numerical model based on homogeneous hydrogen properties. The largest discrepancy lies in the observation of two peaks after fifteen days of charging at the slow heating rates (20 K/h, 35 K/h and 50 K/h) which was not observed at the fast heating rates (600 K/h and 900 K/h). However, the end point of the spectra obtained at the fast heating rates corresponded well with both the modelled curve and the position of the second peak after one day charging. It could be argued that the heterogeneous nature of the duplex microstructure comes more into play when fast heating is applied since the rapid temperature increase led to more hydrogen desorption in the beginning. The heterogeneous model showed that hydrogen essentially leaves the steel at an average desorption rate as well. Similar shapes were observed as obtained for simulations under the assumption of homogeneous hydrogen properties. The ability of treating a DSS as a homogeneous material for diffusion was already suggested by Turnbull et al. [229] based on simulations of permeation data. The authors indicated that at higher temperatures, the shape of the permeation transients could be described by Fick's law. The value for the effective diffusion coefficient found in the present work is in relatively good agreement with those found for permeation experiments considering diffusion occurred perpendicular to the layered microstructure while diffusion tests were performed parallel to the phase lavers in the permeation experiments [240].

Taking into account the clear differences in hydrogen-related properties between austenite and ferrite, the heterogeneous diffusion model was used. The partitioning coefficient between austenite and ferrite was 131.6 (based on 710 wppm and 53% austenite). The charging procedure was applied for three different times, i.e. one day of charging, fifteen days of charging and fully charged. The hydrogen concentration after charging until full saturation was not simulated due to time limitations but constructed based on the phase field. The hydrogen distribution after charging is shown in Figure 4-18 for 1 day and 15 days of hydrogen charging. The simulation of the phase dependent concentration profile after fifteen days of hydrogen charging is shown in Figure 4-19 (a). A continuously increasing total hydrogen concentration was calculated throughout the charging procedure as indicated in Figure 4-19 (b) which is in agreement with the melt extraction experiments (Figure 4-8). Figure 4-20 shows the resulting TDS curves obtained at two different heating rates, i.e. 900 K/h and 50 K/h. For the two peaks of the fifteen days hydrogen charged simulation, an activation energy of 49.0 kJ/mol was found. The first peak of the simulations for one day of charging gave a slightly lower activation energy of 46.2 kJ/mol.



Figure 4-18: Hydrogen distribution in the two-phase microstructure after one day and fifteen days of charging, the results are presented in two different scales to be able to interpret the results of both ferrite and austenite



Figure 4-19: Simulation of the total hydrogen concentration as a function of charging time (Heterogeneous diffusion coefficients from [74, 216])



Figure 4-20: Simulated TDS spectra for different charging times and heating rates: (a) 900 K/h and (b) 50 K/h (Heterogeneous diffusion coefficients from [74, 216])

At the beginning of the simulated TDS curves in the heterogeneous model, an additional peak was observed. This is most likely a result of the intentional design with ferrite at the surface which is not representative for the real material. The average diffusion activation energy calculated from the overlapping first peak in the simulation of one day hydrogen charging was also lower due to the relatively higher ferrite fraction at the surface. It is, however, clear that the small peaks at the beginning of the experimental curves tested at the slow heating rates can be explained by the same phenomenon, i.e. fast diffusion near the surface due to the fraction of hydrogen atoms in ferrite that did not interact with any austenite grain. Further proof is the fact that the additional peak is more clearly distinguishable at 50 K/h than at 900 K/h in the simulations using the heterogeneous model since diffusion can be separated more at slower heating rates [208]. Moreover, the experiments only showed this peak at the slower heating rates.

A phase partitioning coefficient of 131.6 was determined in the heterogeneous model. Turnbull et al. [229] mentioned a maximal solubility ratio of 2500 at 293K. The uncertainty was mainly attributed to the solubility of the ferrite phase where the value for pure iron was used. The given value is therefore considered as the maximal solubility ratio. Zakroczymski et al. [244] mentioned a ratio of 26. The authors, however, noted that their charging conditions were rather mild and that presumably, under more severe charging conditions, higher hydrogen concentrations could be reached.

The microstructure-based model could be further refined by reducing the grain size which would not change the shape of the curve but slightly shift the peak positions. Moreover, the ferrite diffusion coefficient could be increased to obtain the diffusion activation energy that was determined experimentally. Alternatively, trapping in ferrite could be taken into account. This implies that the lattice diffusion coefficient of pure BCC iron is used instead of an effective value and that additional parameters are defined for the trapping sites. However, since the experimental data do not contain desorption peaks from ferrite only, these parameters will be very difficult to determine if different types of traps are

considered. A better option would then be to make a generic bulk alloy of the ferritic phase and study this material separately.

Various events take place during thermal desorption experiments. Figure 4-21 schematically presents the proposed process of hydrogen diffusion and trapping in 2205 duplex stainless steel based on the schematic introduced by Lee et al. [58]. Hydrogen can either diffuse through the ferrite matrix with an activation energy Q<sub>F</sub> of 8 kJ/mol or through the austenite matrix with a diffusion activation energy Q<sub>A</sub> of 51-55 kJ/mol. In the ferrite matrix, various microstructural defects are present, e.g. dislocations, grain boundaries and carbides, which trap hydrogen with desorption activation energies E<sub>D</sub> between 20 kJ/mol and 60 kJ/mol. Similar microstructural defects are present in austenite, however, their desorption energy is lower than the diffusion activation energy of austenite Q<sub>A</sub> in the present material. The energy that needs to be overcome to enter a trapping site E<sub>S</sub> is uncertain and is often set equal to the diffusion activation energy value. This only makes sense for the ferrite case and not for the austenite one. It should also be noted that the interface energy E<sub>A/F</sub> between ferrite and austenite is uncertain. Since austenite grains can be electrochemically charged with hydrogen, the interface energy will presumably not be significantly higher than the austenite diffusion energy.

In the proposed hydrogen trapping/diffusion mechanism, eight different types of microstructural positions where hydrogen can reside can be distinguished during a TDS test (see Figure 4-21). In the charged condition, hydrogen can originally be located in ferrite, either in an interstitial position (H1;H5) or in a microstructural trap (H2;H6). Alternatively, hydrogen can initially be located in austenite, either in an interstitial position (H3;H7) or at a microstructural defect (H4;H8). At the start of a TDS measurement, the interstitial hydrogen atoms in ferrite can readily diffuse to the surface (H1) or first need enough energy to leave a trap (H2). The latter will, usually (in case of a full BCC matrix), lead to a postponed detection of the hydrogen atom in the TDS spectra. Alternatively, hydrogen originally located in ferrite can also enter an austenite island where it is slowed down because of the slow diffusion (H5;H6). Hydrogen originating from an interstitial position or a microstructural defect in austenite can leave the austenite island through diffusion after which it can follow a path through ferrite towards the surface (H3;H4) Lastly, hydrogen originally located in austenite can diffuse through various ferrite and austenite layers (H7:H8). Whether a hydrogen atom was located at a microstructural defect in austenite (H4;H8) or in an interstitial position (H3;H7) does not largely influence its desorption speed, especially when the number of traps is small compared to the number of interstitial positions. It might lead to a slight increase of the average diffusion speed through interstitial positions, i.e. grain boundaries and dislocations might act as diffusion highways in FCC materials [129, 246, 247]. From the experimental curves, an average diffusion activation energy was determined with a value in between the one for diffusion in ferrite and austenite. Since the value is relatively close to the one of austenite, it can be assumed that most hydrogen diffused through several austenitic layers on its way out, i.e. mainly H5-H8. The microstructure (Figure 4-6) also insinuates that a path only through ferrite is difficult to find. Hydrogen trapping in ferrite was not visible from the

#### Chapter 4

experimental results. Hydrogen atoms that are released from traps in ferrite are overruled by the large amount of hydrogen atoms that are released from austenite, i.e. the austenite diffusion peak overlaps with the peaks related to trapping in ferrite. Pu et al. [245] also argued that traps created through deformation of 304 stainless steel (dislocations and martensite) cannot be viewed in the large amount of hydrogen originating from interstitial positions in austenite.

Evaluation of hydrogen trapping in duplex stainless steels appeared not to be possible as was shown by combining experimental results with diffusion models. Microstructural features with desorption activation energies greater than the diffusion activation energy of austenite can presumably be distinguished as a shoulder on TDS curves, however, they were not observed in the duplex stainless steel studied in this work. One could argue that there were only a limited number of deep traps present which could not be separated from the background signal due to the large amount of interstitial hydrogen atoms that diffused out of the steel. Possibly, the temperature range of the TDS experiment was not high enough to detect a high temperature hydrogen detrapping peak. The hydrogen concentration difference between melt results and TDS results could indicate that indeed more deeply trapped hydrogen is left behind in the specimen after the TDS test (> 900°C). The hydrogen concentration difference between melt results and TDS results (evaluated by the integral of the curves) was, however, negligible for the present DSS. Although different types of hydrogen atoms were present after the charging procedure as defined in the schematic in Figure 4-21, hydrogen desorbing from austenite by diffusion determined completely the shape of the experimental TDS spectra. The main effect of the presence of the ferrite phase was an increase of the average diffusion kinetics.



Figure 4-21: Schematic representation of diffusion and trapping in 2205 DSS,  $Q_y$  = austenite lattice diffusion energy,  $Q_a$  = ferrite lattice diffusion energy,  $E_{a\gamma}$  = interface energy,  $E_S^{\alpha,\gamma}$  = saddle point energy,  $E_B^{\alpha,\gamma}$  = trap binding energy and  $E_D^{\alpha,\gamma}$  = trap desorption energy, in ferrite and austenite respectively (based on [208])

## 4.5. <u>Conclusions</u>

Electrochemical hydrogen charging was successfully applied to the UNS S32205 duplex stainless steel. The following conclusions were drawn:

- A total homogeneous hydrogen concentration of approximately 710 wppm and an effective hydrogen diffusion coefficient at room temperature of 9.6E-15 m<sup>2</sup>/s were determined by an analytical fit of Fick's second law to the experimental hydrogen saturation curve comprising of hydrogen concentration obtained after different charging times.
- When high hydrogen concentrations were accompanied with high internal stresses, as inherent to duplex stainless steels, dislocation sources became active and the dislocation density increased both in the austenite and ferrite phase. Slip bands were observed in the austenite phase fraction, which were correlated to dislocation generation and movement.
- A combined experimental and numerical approach was used to increase the insights on the interpretation of thermal desorption spectroscopy data of 2205 duplex stainless steel. Hydrogen desorbed through diffusion with an experimentally obtained equation for the temperature dependent effective hydrogen diffusion coefficient ( $D_{eff} = 3E-7 \exp(-\frac{43400}{RT}) m^2/s$ ), which lies in between the hydrogen diffusion coefficients in ferrite and austenite.
- The large amount of hydrogen atoms originating from and/or passing through an austenite region overruled possible detrapping events. If multiple peaks arose, they were a result of heterogeneous hydrogen charging and all gave rise to the same activation energy. Slower heating rates resulted in an additional small peak at the beginning of the experimental TDS data due to fast diffusion in ferrite.
- Hydrogen trapping in austenite with high activation energies could lead to an additional peak at higher temperatures. It might not be visible because the concentration of trap sites is too small compared to the total hydrogen concentration. Additional peaks that would release at temperatures above 900°C (maximum TDS temperature) were excluded.

# Chapter 5 Hydrogen-induced mechanical degradation and hydrogen-assisted cracking in 2205 duplex stainless steel

#### 5.1. Introduction

The two phase microstructure of duplex stainless steels leads to a very complex deformation behaviour. Ferrite typically deforms by deformation slip due to its high amount of possible slip systems while austenite can deform by different mechanisms such as dislocation slip, twin formation and martensitic transformations depending on the stacking fault energy (SFE) and austenite stability. The SFE and austenite stability on their turn depend on the chemical composition of the alloy and the deformation temperature [248]. Breda et al. [249] and Reick et al. [250] reported that despite the low SFE of the austenite phase in 2205 DSS, the austenite was found to be more stable than other austenitic stainless steels due to the interaction between both phases. Martensitic transformation could be promoted in the presence of hydrogen during straining due to the reduction in stacking fault energy and austenite stability [160]. Although a reduction in SFE and increased planar deformation by hydrogen are generally accepted for austenitic stainless steels, no literature data was found focussing on the austenite phase fraction of a duplex stainless steel. In this chapter, an experimental procedure was, therefore, designed to evaluate the effect of hydrogen on the active deformation mechanisms during straining of electrochemically hydrogen charged 2205 DSS. In-situ and ex-situ hydrogen charging will be compared as well.

Several failures of duplex and super duplex stainless steel subsea components have occurred in the past two decades due to hydrogen embrittlement [251]. In 1998, Elshawesh et al. [252] reported that duplex stainless steels can indeed be embrittled if sufficient hydrogen is introduced in the microstructure. Under cathodic charging, a marked reduction in elongation was observed at room temperature. Other authors similarly reported losses in ductility for hydrogen charged DSS [72, 198, 253]. The severity of the embrittlement depended on the applied charging conditions, the amount of hydrogen present in the steel and the test temperature. The direction of loading with respect to the layered structure of DSS was also found to influence the HE sensitivity. Transverse specimens were more embrittled compared to longitudinal specimens due to the enhanced hydrogen diffusivity [254]. The fracture surface in the presence of hydrogen is reported to show a mixture of facet cleavage fracture in ferrite and cleavage fracture associated with plastic deformation in the austenite phase fraction of 2205 DSS [72].

An important aspect in the HE evaluation is the nucleation and propagation of secondary cracks during straining in the presence of hydrogen, i.e. hydrogen-assisted cracking (HAC). HAC was already described extensively in BCC steels where it is influenced by the microstructure, texture and the balance between reversible and irreversible trapping sites. In austenitic steels, HACs were also observed. Local accumulation

#### HE of 2205 DSS

of hydrogen is an important parameter in the initiation of cracks in austenite as well. The required threshold hydrogen concentration was fairly higher than that needed to initiate hydrogen-assisted cracks in ferrite [151]. Several authors mentioned the preferential nucleation of HACs in the ferrite phase fraction of duplex stainless steels [72, 255, 256, 257]. The austenite phase fraction was, however, also reported to undergo preferential cack initiation in [145]. A challenging complication to the study of HACs in austenitic steels are the martensitic transformations ( $\epsilon$ - and  $\alpha$ '-martensite) that can take place during straining. Especially the formation of  $\alpha$ '-martensite has been reported to cause HAC initiation and assist propagation along its interface due to the inherently lower hydrogen solubility and increased hydrogen diffusivity [138]. It is clearly very relevant to know the most vulnerable locations of a steel microstructure to hydrogen-assisted cracking since this creates the opportunity to improve the material properties with respect to its HE susceptibility. In this chapter, the initiation, propagation and interaction with deformation-induced martensite of HACs in 2205 DSS containing high hydrogen concentrations from electrochemical hydrogen charging will be evaluated with an advanced characterization technique, i.e. electron backscatter diffraction (EBSD). EBSD has proven to be a powerful tool in the study of hydrogen assisted cracks and their interaction with different phases [66, 174].

Finally, the influence of different austenite phase fractions on the HE sensitivity of 2205 duplex stainless steel will also be looked at. In welds for example, the fraction of ferrite can differ from the bulk fraction due to the inability to control the temperature profile. In general, the ferrite fraction should remain in the range of 30-35% to 60-65% [258]. As the ideal phase fraction (50/50) imparts the optimum mechanical properties and corrosion resistance, the HE sensitivity could be impacted as well when the ideal phase balance is not present. Yang et al. [259] stated that the heat affected zone was most prone to HE since this microstructure contained the highest ferrite fraction. The weld material was least embrittled because of its fine microstructure. Similarly, the hydrogen cracking susceptibility was found to increase markedly when the ferrite content increased above 50% for 2205 DSS [260]. In gaseous H<sub>2</sub>, HE susceptibility was also more obvious when the DSS contained a higher amount of ferrite [261]. The effect of the  $\delta$ -ferrite fraction on the HE susceptibility of 304L austenitic stainless steels was investigated by Buckley et al. [262] in the framework of welding as well. The HE sensitivity similarly increased with increasing ferrite fraction.
# 5.2. <u>First observation by EBSD of martensitic transformations due to hydrogen presence during straining</u> of duplex stainless steel<sup>5</sup>

The present study was performed on the as-received UNS S32205 DSS plate characterised in 4.2. The sample surface was prepared by standard metallographic methods including grinding and polishing. This resulted in a tensile specimen thickness of 0.75 - 0.77 mm. The mechanical behaviour was tested by means of constant extension rate tensile tests. The tensile tests were executed at a constant crosshead displacement speed of 0.6 mm/min, which corresponds to a strain rate of 1x10<sup>-3</sup> s<sup>-1</sup>. The uncharged tests were performed in air. These tests were compared to specimens which were hydrogen charged for 24 hours and tested either ex-situ, i.e. in air, or in-situ, i.e. with continuous hydrogen charging during the tensile test. Interrupted tensile tests were additionally designed to compare the active deformation mechanism in the hydrogen charged and air conditions..

Figure 5-1 shows the engineering stress as a function of engineering strain for the uncharged and charged tests. The total hydrogen concentration charged into the steel after 24 hours of charging was 113.8  $\pm$  5.8 wppm as determined with melt extraction on specimens with a thickness of 0.75 - 0.77 mm. Two tests were conducted for each condition, clearly demonstrating its reproducibility. Based on the most critical condition, i.e. the in-situ tested specimens, an engineering strain of 26% was chosen for the interrupted tests to identify the effect of hydrogen on the active deformation mechanism. These interrupted tensile tests are also included in the figure. Hydrogen absorbed in the microstructure of UNS S32205 had a pronounced influence on its macroscopic tensile behaviour. As expected, a distinct loss in ductility and toughness was observed when hydrogen was present [198, 202, 263]. Although hydrogen occupied only a limited region from the surface onwards, the effect on the tensile behaviour was significant. High surface concentrations are thus very detrimental. When hydrogen was continuously charged into the steel during straining, the ductility loss was even more pronounced. Hydrogen can in this case directly adsorb at critical locations in the steel microstructure and cause crack initiation and/or propagation. However, the increased hydrogen concentration applied during the precharging procedure is still required to observe the ductility drop since no ductility drop is present after in-situ straining without precharging. Apart from the ductility loss, hydrogen charging also increased the macroscopic yield stress. Zakroczymski et al. [202] similarly found this strengthening of DSS upon hydrogen introduction with an increasing effect for higher hydrogen concentrations. The authors did not provide an explanation for this observation. The increase might be attributed to hydrogen pinning dislocations (solid solution strengthening) [264, 265] and/or to an increased dislocation density created during charging. Concerning the latter argument, high internal stresses are present in duplex stainless steels as a result of the thermal treatment needed to create equal

<sup>&</sup>lt;sup>5</sup> This subchapter was based on the following publication: L. Claeys, T. Depover, I. De Graeve and K. Verbeken, "First observation by EBSD of martensitic transformations due to hydrogen presence during straining of duplex stainless steel", Materials Characterisation 156 (2019), 109843, <u>https://doi.org/10.1016/</u>j.matchar.2019.109843

phase fractions at room temperature [237]. Upon introduction of hydrogen, dislocation sources start creating new dislocations due to a reduced shear modulus (see Figure 4-9). Moreover, the newly emerged and already existing dislocations migrate in the steel microstructure when hydrogen is present [197]. The increase in yield stress is equal for both hydrogen charged testing strategies indicating that internal hydrogen is responsible for the increase. Both proposed mechanisms can be linked to the observation. Most likely, the reason for the increased yield stress is thus a combination of both mechanisms.



Engineering Strain [%]

Figure 5-1: Engineering stress as a function of engineering strain for uncharged UNSS32205 DSS compared to 24 hours hydrogen charged and in-situ or ex-situ tensile tested specimens

Figure 5-2 shows the EBSD measurements on the ND surface of the interrupted tensile tests. The initial state, without hydrogen charging and deformation, is included as a reference. Both image quality maps and phase maps are shown. The difference in austenite phase fraction on the phase maps compared to the 50/50 ratio can be understood in terms of the investigated plane lying parallel to the elongated structure, which leads to either ferrite richer or austenite richer zones at the surface. Figure 5-3 shows a detailed EBSD measurement of a deformed austenite grain on the interrupted in-situ hydrogen charged specimen. An image quality map, inverse pole figure map and phase map are presented. Moreover, several pole figures are included of specific crystallographic directions with respect to the sample reference system. These were constructed by first creating a partition based on crystal orientation with a maximal deviation of 5°. The orientations are indicated on the inverse pole figure map. High angle grain boundaries (>15°) are indicated in black in both figures.

Clear differences can be observed in the deformation characteristics of the austenite phase. The specimen strained in air had a homogeneously increased dislocation density. In the hydrogen charged conditions, slip planarity was observed in the austenite grains. This was more pronounced in the in-situ tested

specimen as indicated by the white arrows in Figure 5-2. Moreover, martensitic phases were additionally detected in both hydrogen charged cases. For the ex-situ tested specimen, only ε-martensite was detected. For the in-situ tested specimen, the martensitic phases consisted of both ε-martensite, the largest fraction, and α'-martensite inside the formed ε-martensite zones. Although α'-martensite is crystallographically undistinguishable from ferrite in EBSD scans, the location of a BCC phase inside the formed HCP phase, visualised in more detail in Figure 5-3, confirms the assumption that the α'-phase formed during deformation. In both cases, the additional martensitic transformations did not lead to an increase in work hardening. Since the transformation took place in the near-surface region only, the martensite that formed was not able to change the macroscopic tensile behaviour.

Both slip planarity and the formation of martensitic phases can be explained by the inability of dislocations to cross-slip. As there is a general consensus that the SFE can be linked to the appearance of certain microstructural deformation features in FCC alloys [16], a first explanation for the change in deformation mechanism towards more planar slip is a SFE reduction by hydrogen. Stacking faults were therefore studied via TEM. Since stacking faults should be in equilibrium in order to measure their width accurately and correlate this width to the SFE, reliable stacking faults cannot interact with dislocations, other stacking faults or grain boundaries. In the case of interaction with these features, the stacking faults do not develop to their equilibrium length which is determinant for the SFE [266]. For TEM study, the material was strained to 3% in order to create an adequate amount of not interacting splitted dislocations as was also done in the work of Reick et al. [250]. Both uncharged and charged specimens were strained for comparison. Charging lasted for 168 hours to have a larger hydrogen affected region. This is represented schematically in Figure 5-4 showing the normalised hydrogen concentration profile based on a homogeneous diffusion coefficient of 2.2E-14 m<sup>2</sup>/s. Straining of the hydrogen charged specimen was done ex-situ. The location of the thin foil created after charging and subsequent straining is indicated on Figure 5-4 as well. Figure 5-5 shows TEM images of an air strained (a) and hydrogen charged and strained (b) specimen. Various stacking faults were observed. Some of them are indicated by white arrows. In both cases, the stacking faults were very large and interacted with grain boundaries and/or dislocations which made conclusions on their energy not reliable in the present alloy. Reick et al. [250] were, however, able to determine a value for the SFE of a 2205 DSS via dislocation nodes observed with TEM and found 10 mJ/m<sup>2</sup>. The authors did not perform any hydrogen charging to quantify the influence of hydrogen on the stacking fault energy. It was concluded that although the SFE value is rather low, the deformation behaviour was not as expected leading to martensitic phases because ferrite mainly contributed to the deformation at high strains and an increasing number of austenite grains stopped participating in the deformation process at high strain values [249, 250]. It could therefore be argued that in the present hydrogen charged case, ferrite might be embrittled to a large extent leading to more accommodation of plastic strain by the austenite phase and hence martensitic transformations. Together with a reduction of 20-40% in SFE, as indicated in Chapter 2 for austenitic stainless steels, this could explain the large change in observed deformation mechanism. Thirdly, the inability to cross-slip can be explained by the pinning of

edge dislocations by hydrogen atmospheres. Ulmer et al. [151] stated that hydrogen atoms are preferably attracted to the stress field of edge dislocations. Since a transition to the screw type is needed to cross-slip, the pinning of edge dislocations inhibits cross-slip. This hydrogen effect was already shown in aluminium where dislocation cross-slip was halted by the introduction of hydrogen visualised with TEM [267].

Ex-situ tested specimens showed the same tendency towards slip planarity and martensitic transformations as the in-situ tested specimens, however, to a lesser extent. The transformation of ε-martensite to a'-martensite e.g. did not yet proceed in the ex-situ case. All three proposed mechanisms depend on the local hydrogen concentration in the steel microstructure with higher hydrogen concentrations promoting slip planarity and martensitic transformation. During an ex-situ test, hydrogen is able to desorb, resulting in a reduced tendency to transform. During in-situ testing, on the contrary, hydrogen is continuously added to the microstructure leading to an increased tendency to transform.

Finally, a closer look was given to the mechanisms of the martensitic transformations. Crystallographic orientation with respect to the loading direction is a very important aspect for the formation of martensite. Not every austenite grain in Figure 5-2 has an equal tendency to form martensitic phases. The austenite grain in Figure 5-3 contains annealing twins with a different orientation compared to the parent grain that are free of martensite while the parent grain underwent martensite transformations. The formation of  $\epsilon$ martensite happens by the gliding of Shockley partial dislocations on every second {111}, plane [248]. The Shoji-Nishiyama orientation relationship is established between austenite and ɛ-martensite, i.e.  $\{111\}_{//}(0001)_{\epsilon}$  and  $\{110>_{/}/<11-20>_{\epsilon}$  [248, 268]. The former is visualised by the first and third pole figure (Figure 5-3) in which a clear overlap of the [0001] pole with one of the <111> $\gamma$  poles was observed. One single variant of  $\varepsilon$ -martensite was formed in the austenite grain in Figure 5-3. The formation of  $\varepsilon$ martensite is, however, an intermediate step towards the formation of a'-martensite. Yang et al. [268] elaborated on the formation of a'-martensite out of single  $\varepsilon$ -laths during the  $y \rightarrow \varepsilon \rightarrow a'$  martensitic phase transformation in 304 stainless steel. It is energetically preferred to nucleate a'-martensite inside preformed ɛ-martensite laths rather than in the y-matrix. However, in most cases, o'-martensite nucleates at the intersection of two ε-martensite laths and the mechanism is rather well established. Yang et al. [268] concluded that the nucleation in one  $\varepsilon$ -martensite lath follows the same mechanism. Moreover, the Kurdyumov-Sachs orientation relationship is obeyed, i.e. {111}<sub>4</sub>//{0001}<sub>6</sub>//{110}<sub>0</sub>, and <110><sub>4</sub>//<11-20><sub>6</sub>//<111><sub>0</sub>, [248, 268]. The pole figures in the present case show the same trend. The [0001]ɛ pole can be found in all pole figures. The twin orientation relation, i.e. 60°<111>, is established by the shared pole with both martensitic phases.

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Figure 5-2: EBSD measurements showing image quality and phase map on (a) initial state, (b) interrupted tensile test in air, (c) ex-situ interrupted tensile test and (d) in-situ interrupted tensile test, the white arrows indicate planar slip



Figure 5-3: Detailed EBSD measurement on hydrogen charged and in-situ deformed austenite grain. Various pole figures are included



Figure 5-4: Normalized hydrogen distribution over the cross section of the specimen after precharging for 24 and 168 hours, the part of the specimen used as thin foil for TEM is indicated



Figure 5-5: TEM images of stacking faults (some of them indicated with white arrows) after straining of DSS in (a) air and (b) with hydrogen charging (ex-situ tested), A = austenite grain,

F = ferrite grain

# 5.3. <u>Hydrogen-assisted cracking in duplex stainless steel: initiation, propagation and interaction with</u> <u>deformation-induced martensite<sup>6</sup></u>

It is debated in literature whether martensite formation is critical in the explanation of hydrogen embrittlement occurring in austenitic steels. Various authors state that the martensitic transformation is responsible for hydrogen embrittlement [138, 269]. Martensite formation at the crack tip is also stated to aid the propagation of cracks [270]. In contradiction, other authors mentioned that martensite formation is neither necessary nor sufficient to explain the observed hydrogen embrittlement of austenitic steels [271]. In the present work, the interaction of hydrogen-assisted cracks with deformation-induced martensite was, therefore, studied in more detail.

The mechanical behaviour was again evaluated with constant extension rate tensile tests. Similar conditions were used as explained in 5.2, i.e. a final specimen thickness of about 0.75 to 0.77 mm and a constant crosshead displacement speed of 0.6 mm/min, which corresponds to a strain rate of 1x10<sup>-3</sup> s<sup>-1</sup>. Uncharged tests were again performed in air. Hydrogen charged specimens were tested in-situ while hydrogen precharging lasted both for 24 and 168 hours. Figure 5-6 (a) shows the results of the tensile tests performed until fracture in air and after hydrogen charging for one or seven days. Two tests were included for every condition to illustrate the reproducibility of the results. Figure 5-6 (b) shows the hydrogen concentration charged into the steel with a thickness of 0.75 - 0.77 mm for both hydrogen charged conditions as determined with melt extraction. Longer charging times resulted in a larger hydrogen concentration inside the specimen, i.e. 113.9 wppm and 213.3 wppm for the 24 hours and 168 hours hydrogen charged condition respectively. Both charging conditions were, however, unable to homogeneously charge the duplex stainless steel with hydrogen. The high hydrogen concentrations and continuous hydrogen charging during tensile straining induced significant ductility losses (25.6% for 24 hours hydrogen charging and 43.6% for 168 hours hydrogen charging). The ductility loss when a homogeneous hydrogen concentration is present will presumably be even higher. Similar ductility losses for heterogeneously charged 2205 duplex stainless steel were observed in literature. Luu et al. [72] observed a ductility loss of 20% based on the elongation at fracture. Charging was performed for 30 days in 0.05 M H<sub>2</sub>SO<sub>4</sub>. Vanova et al. [253] found an embrittlement index of 30.9-36.7% after one day of hydrogen charging. The authors used a slightly slower strain rate, which increases the susceptibility to hydrogen embrittlement since more time is given for hydrogen to diffuse [50]. Similarly to what was observed in the present work, an increase in ductility loss (from 17% to 52%) when hydrogen charging was performed for longer times (2 days versus 10 days at -1500 mVSCE) was observed by Luo et al. [198]. The increase in ductility loss with increasing charging time is a result of more hydrogen that penetrated deeper into the

<sup>&</sup>lt;sup>66</sup> This subchapter was based on the following publication: L. Claeys, I. De Graeve, T. Depover and K. Verbeken, "Hydrogen-assisted cracking in 2205 duplex stainless steel: initiation, propagation and interaction with deformation-induced martensite", Materials Science and Engineering A 797 (2020), 140079, <u>https://doi.org/10.1016/j.msea.2020.140079</u>

material [50]. Work hardening before fracture was similar for all three tests, i.e. remained unaffected by hydrogen.

The presence of hydrogen in the microstructure increased the macroscopic yield strength of the duplex stainless steel compared to the test in air. The increase was more pronounced for longer charging times and thus higher hydrogen concentrations. Gavriljuk et al. [272] performed ab initio calculations and found that when dislocations are immobile, hydrogen is able to mildly pin dislocations as interstitial atom. This pinning could explain the increase in yield stress for the hydrogen charged specimens. Higher hydrogen concentrations located further away from the surface and as such increase the yield strength more. Apart from the pinning of dislocations, the increase in dislocation density upon hydrogen charging can also explain the increase in yield strength. Longer charging times increase the dislocation density in grains located further away from the surface of the material leading to a larger increase in yield strength [199]. Most likely, the increase can be explained by a combination of both phenomena. Similar increases in yield strength were observed in other works [264, 265].



# Figure 5-6: (a) Engineering stress as a function of engineering strain without (air) and with in-situ hydrogen charging, (b) hydrogen concentration determined by melt extraction after hydrogen precharging

The fracture surfaces of all conditions were investigated with SEM as shown in Figure 5-7. Ductile dimples were observed on the entire fracture surface of the specimen tested in air. A detailed image can be found in Figure 5-7 (b). When hydrogen was present, a brittle region was observed at the edges of the specimen. The brittle zone was characterized by quasi-cleavage fracture as generally observed in hydrogen embrittled steels. It can be correlated to sub-surface intense and highly localised deformation bands which is fully consistent with the hydrogen enhancing localized plasticity theory [273]. A hydrogen embrittled zone at the surface is typically observed for heterogeneously charged steels. Its size depends on the diffusion depth of hydrogen into the material during precharging, the critical hydrogen concentration for a change in fracture surface morphology as well as on the applied strain rate [50]. In

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the centre of the hydrogen charged specimen, dimples were observed with the same characteristics as the dimples observed in the air condition. The size of the brittle zone increased with increasing precharging time since hydrogen penetrated deeper into the material as illustrated in Figure 5-7 (c) and (e). Figure 5-8 shows the theoretical hydrogen concentration profile through the thickness of the tensile specimen for both charging conditions based on Fick's second law (hydrogen diffusion coefficient as determined in 4.4). Although hydrogen reached the centre of the specimen after 168 hours of charging, vet in minimal concentrations, ductile dimples were still observed, i.e. little to no influence of hydrogen in the centre part of the specimen was visible. The size of the brittle zone was added to Figure 5-8 (green vertical lines) indicating that a critical average hydrogen concentration level (red horizontal line) exists where the fracture mode is altered from ductile dimples to quasi-cleavage, i.e. where a clear hydrogen effect is observed. The average critical hydrogen concentration was determined as 250 wppm in the present work. Griffiths et al. [203] similarly stated that the threshold total hydrogen concentration for hydrogenassisted cracking was between 100 wppm and 250 wppm in 22% Cr DSS. Since austenite and ferrite have largely different solubilities and diffusion properties, it is difficult to determine a relationship between the critical hydrogen amount in both phases separately and the size of the zone showing quasi-cleavage. The analysis thus showed qualitatively that the size of the brittle zone could be estimated based on homogeneous hydrogen properties. Cracks were observed in the brittle zone of the specimens as indicated by white arrows in Figure 5-7 (d) and (f). The cracks were more developed after 168 hours hydrogen charging due to higher hydrogen concentrations and the larger zone where the critical hydrogen concentration was reached. In both hydrogen charged conditions, a shear zone was observed in between the brittle region and the ductile dimples. This shear zone was also observed near the edge of the specimen tested in air and is characteristic for ductile fracture [274]. On Figure 5-7 (e), the three different zones are indicated.

The normal surfaces of the fractured specimens were investigated through SEM as well. Figure 5-9 shows these side surfaces for a specimen tested in air and for both one and seven days hydrogen charged specimens. For the test in air, a lot of plastic deformation was observed and no cracks were present on the surface. Hydrogen-assisted cracks were, however, observed on the normal surface in both hydrogen charged conditions. For the one day charged specimen, cracks were observed over the entire section. The cracks increased in size and number close to the fracture surface, i.e. the necked region. A similar observation was made for the seven days charged specimen, however, the more developed cracks were only observed very near to the fracture surface as indicated by the white ellipse in Figure 5-9 (c). The total amount and size of large cracks started initiating. The higher fraction of more developed cracks, that also extended to locations at a larger distance from the fracture surface for 24 hours hydrogen precharging, can be related to the strain level that was reached. The required strain for crack propagation was only reached in the necked region, i.e. where the highest strain values were reached. Due to the earlier

fracture and thus reduced plastic deformation of the seven days charged specimen, crack propagation was less pronounced.



Figure 5-7: Fracture surface characterisation: (a),(b) air test, (c),(d) embrittled region one day hydrogen charged test, (e),(f) embrittled region seven days hydrogen charged test

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Figure 5-8: Critical hydrogen concentration based on theoretical hydrogen concentration profile (Fick diffusion 4.4) for the transition from ductile dimples to quasi-cleavage on the fracture surface of hydrogen charged and in-situ tensile tested 2205 DSS





Several interrupted tensile tests were performed to evaluate the initiation of hydrogen-assisted cracks. In the remaining part of this section, focus will lie on the 24 hours charged specimen since more and larger cracks were observed. All conclusions are also valid for the cracks on the 168 hours charged specimen. Figure 5-10 shows the engineering stress as a function of engineering strain for four interrupted tests after one day hydrogen charging. One of the tests performed until fracture was added to the graph as well. As previously mentioned, austenite can have the tendency to undergo martensitic transformations under the influence of deformation. The presence of hydrogen in the microstructure might also have an influence on the transformation process. It was therefore verified at which intermediate elongation martensite formation starts, on the one hand, and cracks initiate, on the other hand. Figure 5-11 shows phase maps measured on the ND plane (gauge part) of the specimens strained to 11 and 16%. Both images show the presence of epsilon martensite in austenite, however, more pronounced at an elongation of 16%.

Martensite thus started forming in favourably oriented grains already at the early stages of plastic deformation. As a reference, Figure 5-12 indicates that no martensitic transformations were observed at an intermediate elongation of 26% and 40% in air, indicating that hydrogen induced the martensitic transformations upon deformation. Figure 5-13 shows SE images of the ND plane for all intermediate elongations. At an elongation of 11% and 16%, no cracks were observed. As martensite formation already proceeded soon after yielding, there is thus no one on one link between martensite formation and crack initiation in the present hydrogen precharged duplex stainless steel. Several cracks initiated at an elongation of 21% as indicated by the white ellipses in Figure 5-13 (21%). The number of initiated cracks increased for the 26% elongated specimen compared to 21% of elongation. The average crack length increased slightly from 21% to 26% elongation as well.



Figure 5-10: Engineering stress as a function of engineering strain for four different interrupted tensile tests on 24 h precharged 2205 DSS



Figure 5-11: EBSD characterisation (phase map) of ND surface after straining of one day hydrogen charged 2205 DSS to an intermediate elongation of 11% (a) and 16% (c), (b) shows a detailed image of the zone within the white rectangle in (a), formation of epsilon martensite indicated by white circles in (c)



Figure 5-12: EBSD characterisation (phase map) of ND surface after straining in air to an intermediate elongation of 26% (a) and 40% (b)



Figure 5-13: SE images of ND surface after straining of one day hydrogen charged 2205 DSS to an intermediate elongation of 11, 16, 21 and 26%. Cracks form in a later stage (>16% elongation)

Hydrogen-assisted cracks were studied with SEM and EBSD to identify the microstructurally most prone regions for crack initiation. Figure 5-14 (a) shows an image of several cracks in which the initiation characteristics were identified based on the phase map and ND inverse pole figure (IPF) map, Figure 5-14 (b) and Figure 5-14 (c) respectively. On these maps, the cracks were visualised in black based on their low image quality. The phase maps indicated in which phase the crack initiated while the ND inverse pole figure maps indicated whether the crack initiated on a grain boundary or inside a grain. Cracks which were small enough to stay within one phase or boundary were used for the determination of the most favourable initiation site. Over 50 cracks were analysed and 43 were included in the graph (exhibiting clear initiation) to be statistically relevant. Different categories were chosen based on the observed cracks: austenite grain interior, austenite/austenite grain boundary, austenite/martensite interface, ferrite grain interior or austenite/ferrite interface. Figure 5-15 gives a schematic representation of the percentage of cracks that initiated at the mentioned microstructural locations. The colour code distinguishes between cracks located in austenite, ferrite or at their interface.

The EBSD study revealed that most of the cracks initiated in austenite (78.7%). The transformed martensite phase was not particularly prone to hydrogen-assisted cracking. Some cracks were observed on the interface between austenite and martensite. It should, however, be noted that it is unclear whether the interface was already there when the crack nucleated or whether the martensitic transformation approached the crack after its nucleation. Literature on austenitic stainless steels also indicated that strain-induced martensite is neither required nor sufficient for hydrogen-assistant fracture. Indeed, explanations invoking the role of martensite cannot explain the observed trend of hydrogen-assisted fracture in austenitic stainless steels [271]. Preferential crack initiation in the transformed martensite phase of TRIP steel might be related to the type of martensite that formed since a'-martensite was detected there [174]. In the present work, a'-martensite was detected in a very minor fraction in a later stage (26% elongation) and was embedded in the ε-martensite laths, i.e. mainly ε-martensite/α'martensite interface was created and no austenite/o'-martensite interface was formed. No crack initiation or propagation was observed in or at the formed g'-martensite. Crack initiation in ferrite and at the interface between ferrite and austenite happened less frequently in the present duplex stainless steel, 16.6% and 4.7% of the cracks respectively. Possibly, austenite acted as a hydrogen sink, continuously extracting hydrogen from ferrite since the material was not yet homogeneously charged with hydrogen during the tensile test. Austenite can thus be compared to irreversible traps where hydrogen is accumulated but which can also serve as crack initiation sites at specific critical concentrations.

Crack initiation in austenite was observed by Li et al. [145] as well. The authors studied hydrogen-assisted crack initiation in duplex stainless steel that already showed martensitic transformation when straining in air at room temperature. The hydrogen charging conditions were very similar to the conditions used in this work. Cracks nucleated in austenite at locations where, locally, high hydrogen concentrations were present. The  $\gamma/\epsilon$ -interface provided high resistance to crack nucleation in their work, as was also observed

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in the present work, which the authors explained by the high surface separation energy of such an interface. Contradictory to the present work, some authors have observed favourable crack initiation in ferrite. Hydrogen-assisted cracks preferentially initiated in the ferrite phase and were stopped or deflected by the austenite phase. Cracks in ferrite showed a typical brittle cleavage and were able to induce a micro-crack in austenite after which it propagated via the formed micro-crack [72, 255, 256, 257]. The mentioned literature used either artificial sea water and other low intensity electrolytes that were most likely not able to charge high hydrogen concentrations in the austenite fraction within the applied charging time or did the tests in air without in-situ absorption of hydrogen at vulnerable locations. The conditions in this work were rather severe to allow an accelerated test procedure and induced a large amount of hydrogen in austenite both before and during the test. High hydrogen concentrations result in slip localisation in the austenite phase. Slip bands already started appearing during the electrochemical charging procedure as was shown in Figure 4-9. The internal stress and the stress exerted by hydrogen on the lattice were sufficient for the nucleation and migration of dislocations. When external stress is additionally applied, planar slip continues to take place in the hydrogen affected austenite grains. Due to the restricted ability for dislocations to cross-slip under the presence of hydrogen, formation of martensitic phases becomes an important deformation mechanism as well. Localisation of deformation in bands facilitates the nucleation of voids at the intersection of deformation bands. Moreover, hydrogen tends to decrease the distance between dislocations in dislocation pile-ups as such increasing the stress level associated with the pile-up. At these intersections and stress concentrations, a microvoid embryo nucleates which then serves as crack initiation site. The high hydrogen concentration in the austenite grains is therefore a critical prerequisite for the preferential crack initiation in austenite [151, 275]. It is expected that in practical situations, the very large hydrogen concentrations to induce the phenomena observed in the present work can be attained locally in the structure after exposure to hydrogen containing environments for prolonged times.

Most of the cracks that initiated in austenite had a very straight character while the cracks that initiated in ferrite were S-shaped. A detailed image of a straight crack in austenite can be seen in Figure 5-16. Figure 5-16 (a) shows a phase map with an image quality (IQ) overlay and Figure 5-16 (b) shows an ND inverse pole figure map with an IQ overlay. Two active slip systems were observed based on the overlaying IQ map (indicated by white lines).  $\varepsilon$ -martensite was formed aligned with one of the slip lines, through overlap of partial dislocations on every second {111}<sub>y</sub> plane. The crack did not initiate aligned with one of the slip lines but inclined to both lines.



Figure 5-14: EBSD characterisation of HACs on the ND plane after straining of one day hydrogen charged 2205 DSS to an intermediate elongation of 26% (a) SE image with indication of type of crack (A= austenite, F= ferrite, M = martensite, IF = interface and GB = grain boundary), (b) phase map and (c) ND IPF map



Figure 5-15: Fraction (%) of cracks initiating at specific microstructural features (A= austenite, F= ferrite, M = martensite, IF = interface and GB = grain boundary)

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# Figure 5-16: EBSD characterisation of HAC initiation on ND plane after straining of one day hydrogen charged 2205 DSS to an intermediate elongation of 26%. (a) Phase map and IQ map overlay, indication of slip lines, (b) ND IPF map and IQ map overlay

Hydrogen-assisted crack propagation was studied with SEM and EBSD similarly to how initiation sites of the hydrogen-assisted cracks were identified. Further evaluation will focus on one day hydrogen charged specimens since many developed cracks were observed near the fracture surface, cf. Figure 5-9 (b). The propagation of cracks on the seven days charged specimen had similar characteristics. Figure 5-17 and Figure 5-18 show EBSD measurements performed on propagated cracks. The cracks propagated both through ferrite and austenite grains. No clear preference could be identified. The interface between austenite and ferrite acted as a propagation path as well, although transgranular crack propagation appeared to be the most favourable.

Clear interaction between cracks was observed, i.e. the crack tips deflected towards each other. Deflected crack tips also coalesced to form one larger crack, i.e. crack propagation through interconnection of smaller cracks. In many cases, this led to an inclusion of material in between the two interconnected crack tips. Both Figure 5-17 and Figure 5-18 clearly show material islands in between coalesced cracks. All cracks were oriented perpendicular to the loading axis. The straight cracks in the austenite phase were often slightly inclined depending on the crystallographic orientation of the parent austenite grain. Cracks that initiated in ferrite or larger cracks than the straight ones in austenite showed the typical S-shape as was also observed in other works dealing with hydrogen-assisted cracking [66, 174, 276]. The deflection of crack tips from their main propagation path can be explained by the interaction of the crack tip with the strain field of other cracks or notches. The main factor controlling the propagation trajectory of the hydrogen-assisted crack is thus the local strain distribution [277]. No distinction was made between the phases for the propagation of the cracks. Crack tip deflection occurred both through austenite grains and ferrite

grains and eventually resulted in the combination of several smaller cracks into one large crack. In the final stage of the tensile test, several large cracks combined leading to complete fracture. The coalescence of parallel cracks often led to material islands in between crack tips, as was also described by Laureys et al. in TRIP steel [174].



Figure 5-17: EBSD characterisation of propagated HACs on ND plane after straining to fracture of one day hydrogen charged 2205 DSS (a) SE image, (b) phase map and (c) ND IPF map



Figure 5-18: EBSD characterisation of propagated HACs on ND plane after straining to fracture of one day hydrogen charged 2205 DSS (a) SE image, (b) phase map and (c) ND IPF map

# 5.4. Evaluation of the hydrogen embrittlement sensitivity of duplex stainless steel with different phase fractions<sup>7</sup>

Usually, ferrite and austenite are present in equal fractions in commercial DSS to obtain an optimal combination of mechanical properties. An austenite phase fraction that differs from this ideal 50% is, however, relevant in welded structures. The aim of this work was therefore to study the influence of the austenite phase fraction on the hydrogen embrittlement sensitivity of 2205 DSS. First, two heat treatments were performed in order to create DSS samples with a different austenite phase fraction. Thereafter, constant extension rate tensile tests were performed both with and without the presence of hydrogen. The tests without hydrogen were performed in air and the tests with hydrogen were performed in-situ, using 24 hours hydrogen precharged specimens. The tests were again performed at a constant crosshead displacement speed of 0.6 mm/min, which corresponded to a strain rate of 1E-3 s<sup>-1</sup>. Tensile tests were also interrupted before fracture (stopped at an elongation where the ultimate tensile strength (UTS) was just reached) to study hydrogen-assisted cracking on the sample surfaces.

The steel was subjected to two different heat treatments in order to create materials with a differing austenite fraction: one with equal fractions of ferrite and austenite, and another with approximately 40% austenite. The samples were heated to a temperature were the desired phase balance was present, followed by quenching in a brine solution (7 wt% NaCl). The heat treatments were executed in a resistance furnace (Nabertherm). The required annealing temperatures were chosen based on Thermocalc calculations (see Figure 4-2) as 1190°C and 1110°C for the 40% austenite and 50% austenite, respectively. Annealing times were selected to ensure similar grain sizes in both heat treated materials since grain size influences both the hydrogen behaviour of a material as well as its mechanical properties. 10 min was selected for the samples annealed at 1190 °C and 30 min was chosen for the samples annealed at 1110 °C. The resulting two heat treated materials will be referred to as HT 1190 and HT 1110 in the following sections.

Optical microscopy (Figure 5-19) revealed a strongly oriented microstructure as a result of hot rolling. On the longitudinal section (TD plane) elongated austenite grains (light colour phase on Figure 5-19) were observed parallel with the rolling direction, embedded in a ferrite 'matrix' (darker colour phase on Figure 5-19). The samples were free of intermetallic sigma phase, which may precipitate during heat treatment of DSS [278]. The average grain diameter on the TD plane was  $5.18 \pm 0.51 \mu m$  for HT 1190 and  $4.42 \pm 0.34 \mu m$  for HT 1110. The phase balance in both heat treated samples, determined by EBSD and Feritscope measurements, is given in Table 5-1. Magnetic measurements (Feritscope) were considered to be more reliable since they measure a relatively large volume of material compared to EBSD, which is a 2D

<sup>&</sup>lt;sup>7</sup> This subchapter was based on the following publication: M. Cauwels, L. Claeys, T. Depover and K. Verbeken, "The hydrogen embrittlement sensitivity of duplex stainless steel with different phase fractions evaluated by in-situ mechanical testing", Frattura ed Intregrità strutturale 14 (2019), pp. 449-458, <u>https://doi.org/10.3221/IGF-ESIS.51.33</u>

technique and might therefore not be representative for the entire specimen. The HT 1110 sample had an austenite phase fraction close to the intended 50%, while the HT 1190 sample had an austenite content of about 44%.

	HT 1190	HT 1110
EBSD	39.20 ± 2.40	46.10 ± 1.09
Feritscope	43.91 ± 1.15	49.83 ± 0.95

Table 5-1: Average austenite fraction for the two heat treatments, as measured by EBSD and Feritscope



Figure 5-19: Optical microscopy images of the TD plane of (a) HT 1190 and (b) HT 1110, etching with carpenters etchant

Figure 5-20 shows the engineering stress-strain curves for the samples tested in air (full lines) and for those tested 24 hours of hydrogen precharging (dotted lines). Although some experimental variation can be detected on the mechanical data, trends are still reproducible and valid for further evaluation. A possible explanation for the experimental spread is the microstructural nature of the heat treated DSS materials. Since the samples tested were only 0.65 mm thick, this increased the possibility of having different amounts of austenite at the edges where hydrogen is entering the material. Additionally, because of the quenching procedure after the heat treatment, the tensile specimens were geometrically distorted. This distortion also influenced the reproducibility of the results. For the tensile tests performed in air, the elongation at fracture increased with an increased austenite phase fraction. This is to be expected since austenite is more ductile compared to ferrite. The ultimate tensile strength of both heat treated materials was similar.



Figure 5-20: Stress-strain curves of samples tested in air (full lines) and with in-situ hydrogen charging after 1 day of hydrogen pre-charging (dotted line) for both heat treated materials (HT 1190 and HT 1110)

Hydrogen charging had a clear effect on the tensile behaviour of the material. For both heat treatments, there was an evident loss of ductility, seen in the reduction of the total elongation at fracture. Based on the elongation at fracture in air and in hydrogen charged condition, an embrittlement index of 43.3% for HT 1190 and 36.5% for HT 1110 was determined. This is in agreement with other findings in literature since ferrite is considered more susceptible to hydrogen embrittlement than austenite and the HT 1190 material contains the highest ferrite fraction [202, 225, 259, 260, 261]. Moreover, Örnek et al. [279] found that DSS microstructures with a large austenite spacing were more sensitive to HE. The spacing of the austenite grains was larger in the HT 1190 sample, both on account of it having a lower austenite fraction and a slightly larger grain size as seen in Figure 5-19. HT 1190 also had a higher hydrogen concentration than HT 1110 after 24 hours of hydrogen charging. Melt extraction on specimens with a thickness of 0.65 mm measured a hydrogen concentration of 113.9 wppm for HT 1110 and 152.2 wppm for HT 1190. Zakrocymski et al. [202] found that the severity of HE in DSS increased with higher hydrogen concentrations. The decrease in ductility was significant, even though the specimens were not homogeneously charged with hydrogen after 24 hours of hydrogen precharging and thus hydrogen was not present throughout the entire thickness of the specimen. When a homogeneous hydrogen concentration is reached, it can be expected that the HT 1110 will contain a higher hydrogen concentration than HT 1190 due to the higher austenite fraction. The observed trends in the EI could, therefore, be reverse in this condition.

The yield stress of both heat treated materials increased in the hydrogen charged condition. This effect was more pronounced for HT 1190. The increase of the yield strength after hydrogen charging was also

observed in other works, such as in [202] for DSS and in [280, 281] for austenitic stainless steels. The strengthening effect of hydrogen can be attributed to a combination of the pinning of dislocations by hydrogen (solid solution strengthening [264]) and an increased dislocation density from the charging procedure [197]. Both effects may be increased in the HT 1190 samples compared to the HT 1110 samples due to the higher hydrogen concentration in those samples.

The fracture surface of both materials tested in air showed dimples. A lot of necking occurred for both samples, resulting in a very thin fracture surface due to the large reduction in area. Figure 5-21 (a) shows the fracture surface delineated by white lines. The fractured specimens also had a cup-and-cone-like appearance. This, as well as the presence of dimples on the fracture surface, indicates a ductile fracture behaviour in air. In the presence of hydrogen (Figure 5-21 (b)), the appearance of the fracture surface was clearly different. Near the edges of the sample, brittle fracture features were observed. In the centre, ductile fracture features such as dimples were observed. In between, a transition shear zone was observed. On Figure 5-21 (c), the dashed line indicates the size of the brittle zone. This distinct fracture surface is a consequence of hydrogen not being present throughout the entire thickness of the sample after 24 hours of hydrogen precharging.

Figure 5-22 shows the embrittled zone in detail for both heat treatments. These images show a combination of quasi-cleavage and intergranular fracture features. Quasi-cleavage is used to refer to features on a fracture surface that exhibit characteristics of both plastic deformation and cleavage. For quasi-cleavage, the fracture surface has the appearance of a cleavage fracture, but is not along a known cleavage plane [273]. This is an often observed feature for fracture of ferrous alloys which are susceptible to HE [282]. Quasi-cleavage is often characterised by fine lines that follow the crack propagation direction called 'river markings' as indicated by the red arrows in Figure 5-22 (a). A small part of the brittle features for both heat treated samples was intergranular. The HT 1110 sample was seemingly more prone to intergranular cracking than the HT 1190 sample. The reason for the appearance of intergranular cracking that was not observed in the as-received 2205 DSS might be sensitisation of the grain boundaries during the heat treatment [283].

After 24 hours of hydrogen pre-charging, the samples were not homogeneously charged with hydrogen. The depth of the area affected by hydrogen was measured on several SE images and averaged out resulting in a depth of embrittlement of 66.78 ± 1.8 µm for HT 1190 and 56.43 ± 0.8 µm for HT 1110. The average diffusion coefficient of hydrogen in DSS depends on the austenite fraction, as well as the shape, size and spacing of the austenite and its orientation in relation to the direction of hydrogen entry into the material. The lower austenite fraction and larger grain size of HT 1190 contribute to a less tortuous path for hydrogen diffusion could also explain why HT 1190 showed a higher hydrogen concentration after 24 hours of hydrogen charging although it had a lower austenite fraction compared to HT 1110.

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Figure 5-21: Fracture surface for a HT 1190 sample tested (a) in air, (b) and (c) in hydrogen charged condition. (c) shows the depth of the brittle zone (white dotted line) and the direction of hydrogen entry (white arrows)



Figure 5-22: SE images of the embrittled zone in sample (a) HT 1190 and (b) HT 1110. Arrows indicate examples of river markings

Secondary cracks on the ND surface were further examined on tensile samples that were stopped at an intermediate elongation at which ultimate tensile strength was just reached. The cracks were primarily transgranular. Similarly as in 5.3 on the non heat-treated 2205 DSS, many cracks initiated in the austenite phase. This can again be linked to the high hydrogen concentrations precharged to the steels that lead to slip planarity and stress concentration in the austenite phase. For both HT 1190 and HT 1110, cracks across the austenite/ferrite interface were often present as well as cracks that initiated in the ferrite phase. Oltra et al. [284] proposed a mechanism for hydrogen-assisted cracks in DSS that cross a phase boundary. Cracking was stated to start with brittle cleavage in ferrite, which induces a micro-crack in the adjacent

austenite grain when it reaches the austenite/ferrite boundary. This allows a supply of hydrogen from the ferrite to the austenite phase at the crack tip and particularly along slip planes. Local hydrogen accumulation increases dislocation mobility leading to pile-ups ahead of the enhanced plasticity zone [285]. At a critical stress, a new crack is formed at the pile-up and the hydrogen crack can begin to propagate from the initial micro-crack. The sequence can then start again at the new crack, and this process can be expected to lead to regular changes in crack plane. Some of the cracks in Figure 5-23 (a) are examples of cracks that most likely propagated via this proposed mechanism.

Zigzag cracks were observed in austenite. An example of such a crack in an austenite grain in HT 1190 is indicated on Figure 5-24 (a) with a white arrow. The shape of this crack can be a consequence of the microcracks alternating different slip planes while it propagates [284]. Alternatively, Koyama et al. [286] described hydrogen-assisted cracks in an austenitic steel occurring along primary and secondary twins also resulting in a zigzag pattern. Finally, Figure 5-24 (b) shows cracking around inclusions. The inclusions were identified as aluminium oxides with EDX, which can originate from the de-oxidation step in the steel production process, where aluminium is added. Inclusions are typically very prone to hydrogen damage initiation [287].



Figure 5-23: Secondary cracks on the ND surface of a HT 1110 tensile sample



Figure 5-24: Secondary cracks on the ND surface of tensile samples: (a) zigzag crack (indicated by the white arrow) in an austenite grain in HT 1190, (b) hydrogen cracks around alumina inclusions in HT 1110

## 5.5. <u>Conclusions</u>

The influence of hydrogen on the mechanical properties of 2205 DSS was evaluated. Several conclusions were drawn:

- Introduction of hydrogen resulted in a large ductility drop and an increase in yield strength. Longer charging times (168 hours versus 24 hours) increased the effect of hydrogen.
- The critical hydrogen concentration for brittle quasi-cleavage fracture was 250 wppm.
- Planar slip and both ɛ- and ɑ'-martensite were detected in the austenite phase of the hydrogen charged specimens being more pronounced when in-situ tensile testing compared to ex-situ tensile testing. Both phenomena were absent in the case of uncharged specimens. This could be explained by a reduction in the SFE accompanied with a shift in which phase accommodates most of the plastic deformation. Also, the additional pinning of edge dislocations by hydrogen atmospheres inhibiting cross-slip contributed to the large difference in observed deformation mechanism. The austenite to martensite transformation happened in correspondence to established mechanisms.
- Hydrogen-induced martensitic transformations proceeded soon after yielding. However, only at a further stage, when higher strain levels were reached, hydrogen-assisted cracks initiated as well. Due to the high hydrogen concentrations present in austenite, slip localisation introduced stress concentrations which were very prone to crack initiation.
- An EBSD study confirmed that the largest fraction of cracks initiated in austenite. No clear role
  of martensite could be identified., i.e. ε-martensite formation was not prone to crack initiation.
- Crack propagation occurred through austenite, ferrite and their interface and was mainly driven by strain fields. Crack coalescence forming a larger crack was a major propagation mechanism as well.
- Heat treatments were performed on the 2205 DSS to create two materials with an austenite fraction of 50% and 44%. Both heat treated samples suffered a considerable loss in ductility after hydrogen charging. For the 50% austenite specimen, the elongation at fracture was reduced by 36.5%. For the specimen with 44% austenite, this was 43.3%. The loss of ductility was thus greater for the sample with a higher ferrite content. This microstructure had a higher hydrogen concentration and a higher hydrogen diffusion coefficient after heterogeneous hydrogen charging, contributing to its increased sensitivity. Fracture surfaces of specimens tested under the presence of hydrogen showed brittle fracture features on the edges. The depth of the zone with brittle features was related to the diffusion speed of hydrogen. Hydrogen assisted cracking was observed on the side surfaces of specimens tested with hydrogen and appeared to be primarily transgranular.

# Chapter 6 Critical evaluation of the hydrogen interaction with 304(L) austenitic stainless steel

## 6.1. Introduction

Austenitic stainless steels (ASS) are second generation advanced high strength steels. They have been available for about one century [288]. They combine a high ultimate tensile strength with a large elongation at fracture. Due to the alloying with chromium and nickel, stainless steels exhibit excellent corrosion resistance as well. AISI 304 ASS is one of the most used alloys containing approximately 18% of chromium and 8% of nickel [289]. Austenitic stainless steel types are typically further subdivided by their carbon content. 304 ASS and 304L ASS are very similar in chemical composition, however, the carbon content is lower for the 304L ASS (0.03 wt% max). The lower carbon content leads to a small but noticeable reduction in mechanical performance. The steel is, however, more corrosion-resistant when welded due to the minimisation or even elimination of carbide precipitation. The AISI 304 grades are major food processing materials because of their high corrosion resistance and easy formability [290]. Moreover, AISI 304 ASS and 304L ASS are used in construction and automotive industry. A big advantage is their large energy absorption capacity as needed in case of a crash [291]. 304 and 304L ASS are, therefore, often used in bumpers but are also found in fuel tanks, exhaust systems, rotors and luggage racks [292]. Due to their corrosion resistance, many applications are also found in petrochemical, nuclear and corrosive chemical environments.

304 and 304L austenitic stainless steel were confirmed to be sensitive to hydrogen embrittlement. The steels can come into contact with hydrogen during production and while in-service, e.g. due to corrosion processes. Austenitic stainless steels are also popular materials for hydrogen engines, transport and storage applications. Metastable austenitic stainless steels such as 304 and 304L ASS are typically more sensitive to hydrogen embrittlement compared to more stable stainless steel types due to the formation of a'-martensite during deformation. Sensitized 304 stainless steel was also found to be more sensitive to hydrogen embrittlement due to the chromium and carbon depleted zones which are more prone to martensitic transformation [293].

Diffusion of hydrogen towards vulnerable locations in the microstructure is an important aspect in hydrogen embrittlement. Due to the metastability of the austenite matrix in 304 and 304L ASS, the average hydrogen diffusivity is altered when the material is deformed. a'-martensite introduces a fast pathway for hydrogen since it has a much higher hydrogen diffusion coefficient compared to austenite. Various authors determined hydrogen diffusivities with and without prior cold deformation introducing a'-martensite for 304 and 304L ASS through gaseous hydrogen permeation. Table 6-1 summarises the pre-exponential factors D<sub>0</sub> and the diffusion activation energies Q reported in literature as determined by gaseous

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hydrogen permeation. The a'-martensite fraction that was detected in the steel when cold deformation was applied, is added to the table as well. The temperature range in which the values were validated is also given. The general trend shows an increased hydrogen diffusivity with the application of cold work which is attributed to the presence of a'-martensite. 304 and 304L ASS show comparable hydrogen diffusivities as a function of temperature. At room temperature (298 K), annealed 304(L) ASS has an effective hydrogen diffusivity of 1E-16 m<sup>2</sup>/s.

Туре	Condition	a'-martensite	$D_0 [m^2/s]$	Q [kJ/mol]	Temperature	Source
					range ["C]	
304	Annealed	0	6.43E-7	53.45	200-400	[294]
304	Cold deformed 36%	5.6	2.91E-7	45.89	200-400	[294]
304	Annealed	0	7.69E-7	53.3	200-350	[71]
304	Cold rolled 50%	9.5	4.94E-8	40.0	200-350	[71]
304	Annealed	0	1.22E-6	54.67	370-690	[295]
304L	Annealed	0	3.14E-7	53.92	400-700	[296]

Table 6-1: Hydrogen diffusivity of AISI 304(L) ASS in different conditions (annealed or cold deformed) determined through gaseous hydrogen permeation experiments

In this chapter, the hydrogen interaction with 304 and 304L austenitic stainless steel will be evaluated using different approaches. Both electrochemical and gaseous hydrogen charging will be used. The knowledge that was obtained on the analysis of thermal desorption spectroscopy data for materials exhibiting a low intrinsic hydrogen diffusivity in Chapter 4 will be applied to the materials studied in this chapter as well. This approach serves as an alternative technique for the determination of hydrogen diffusion data via the gaseous hydrogen permeation technique for which the values were reported in Table 6-1. The approach is suitable for materials that have not reached a homogeneous hydrogen concentration after charging, which is in particular useful for electrochemical charging procedures. The influence of prior cold work on the hydrogen absorption and diffusivity will be evaluated as well.

# 6.2. <u>Influence of cold work on the hydrogen interaction with 304L ASS after electrochemical hydrogen</u> <u>charging<sup>8</sup></u>

An AISI 304L austenitic stainless steel plate was used for this study with an initial thickness of 0.9 mm. The composition of the steel as provided by the manufacturer can be found in Table 4-1. This stainless steel grade has a nickel equivalent of 11.7 wt% and a chromium equivalent of 21.6 wt%. On the Schaeffler diagram as introduced in Chapter 4, this composition can be found within the austenite and delta-ferrite region after annealing at 1050°C, cf. Figure 6-1, with a total delta ferrite fraction of about 10%. Annealing at higher temperature leads to a negligibly small ferrite fraction after quenching to room temperature resulting in a fully austenitic microstructure. The 304L ASS has, however, a metastable austenitic structure upon deformation at room temperature. The  $M_{d30}$  temperature is about -5°C.

Table 6-2: Chemical composition of AISI 304L ASS<sup>9</sup>

Wt%	C	Cr	Ni	Мо	Mn	Si	Other
UNS S32205	0.025	18.05	8.05	0.32	1.81	1.54	Cu 0.33, P 0.031,
							C0 0.151, N 0.07



Figure 6-1: Schaeffler diagram showing the stable phases after heating to 1050°C for 30 minutes and quenching in water ( [217] adapted from [219]), 304L is indicated in red

Two different material conditions were studied in the present work. The first condition was the as-received 304L ASS. For the second condition, the as-received steel was prestrained to 30% engineering strain in air in a tensile bench at a constant engineering strain rate of 1E-3 s<sup>-1</sup>. Plates (140x40x0.9 mm<sup>3</sup>) were used for

<sup>&</sup>lt;sup>8</sup> This subchapter was based on the following publication: L. Claeys, I. De Graeve, T. Depover and K. Verbeken, "Impact of hydrogen and crosshead displacement rate on the martensitic transformations and mechanical properties of 304L stainless steel", Theoretical and applied fracture mechanics 113 (2021), pp. 102952, https://doi.org/10.1016/j.tafmec.2021.102952

<sup>&</sup>lt;sup>9</sup> Aperam Genk is acknowledged for the received material.

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this purpose. The tensile direction was parallel to the rolling direction of the steel plate. The elongation was determined based on the crosshead displacement and hence does not represent the true plastic strain.

A representative EBSD measurement of the as-received microstructure is shown in Figure 6-2 (a) and (b). The as-received 304L ASS was fully austenitic apart from some residual delta ferrite (< 1%). The grains were equiaxed with an average grain size of  $4.33 \pm 1.77 \mu m$ . Several annealing twins were present. Figure 6-2 (c) and (d) show a representative EBSD measurement of the prestrained 304L ASS. Due to the tensile prestraining at room temperature, deformation-induced a'-martensite was formed, while no  $\varepsilon$ -martensite was detected. Deformation of 304L ASS at room temperature predominantly results in the direct  $\gamma \rightarrow a'$  transformation in addition to dislocation-related processes [297]. The a'-martensite islands were evenly dispersed through the material. Based on the area fraction, an average martensite fraction of 5.6 % was determined with EBSD.



Figure 6-2: EBSD characterisation (ND IPF map and phase map) of as-received AISI 304L ASS in (a) and (b) and prestrained AISI 304L ASS in (c) and (d)

XRD measurements were additionally performed to verify the martensite volume fraction in the prestrained material. The XRD device was operated with a Mo source. The angle 20 was scanned from 25° to 40° with a step size of 0.006° and 5 s holding time per step. Figure 6-3 shows the XRD results for the as-received and prestrained 304L ASS. The measurements showed the appearance of small peaks that could be linked to a BCC phase in the prestrained material which were completely absent in the as-received 304L ASS. Moreover, a slight peak shift of the FCC peaks towards lower angles was observed for the prestrained 304L ASS. The latter can be explained by the residual stresses that appeared in the austenite matrix after prestraining due to the volume expansion of a'-martensite compared to austenite (1.5% to 3.5% according to calculations in [196]). The formula of Cullity was used to determine the phase fraction of martensite in the prestrained AISI 304L ASS. A martensite fraction of 4.8 vol% was found, which is in close agreement with the value found by EBSD.



Figure 6-3: XRD measurements on as-received and prestrained 304L ASS

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Hydrogen was introduced in the 304L ASS through electrochemical hydrogen charging at room temperature for seven days in the sulphuric acid solution introduced in Chapter 3. The effect of the hydrogen charging procedure on the microstructure was checked since many authors mentioned phase transformations taking place during electrochemical hydrogen charging [158, 298, 299]. In the present work, many slip bands were observed on the surface of seven days hydrogen charged as-received 304L ASS, as can be seen in Figure 6-4. The slip bands occurred in straight, parallel lines and are a result of plastic deformation due to the combination of hydrogen (lowers the shear modulus [197]) and internal stress. In most cases, more than one of the {111}<110> slip systems was activated since slip lines were observed in different directions within one grain. No martensitic transformations were observed as checked with EBSD for a larger scanned area (see Figure 6-4 (b)). The pre-existing martensite fraction in the prestrained 304L ASS was also not changed after seven days of electrochemical hydrogen charging. More in depth hydrogen characterisation techniques were subsequently used to compare the interaction with hydrogen for the as-received and prestrained 304L ASS.



# Figure 6-4: Surface appearance after seven days of electrochemical hydrogen charging for as-received 304L ASS (a) SE image showing slip bands without additional surface treatment and (b) phase map

Melt extraction was used to determine the total hydrogen concentration present in both materials after seven days charging at room temperature. The specimens had a thickness of 0.7 mm to be able to link the results to the mechanical tests that will be reported in the next chapter. The melt extraction tests resulted in  $50.0 \pm 2.2$  wppm and  $54.7 \pm 0.5$  wppm hydrogen for the as-received and prestrained 304L ASS, respectively. The slightly higher hydrogen concentration in the prestrained material was most likely a result of enhanced hydrogen diffusion due to the presence of about 6% martensite. The difference is, however, not significant. When a homogeneous hydrogen concentration would be reached, the prestrained material is expected to have a lower hydrogen concentration due to the lower solubility of a'-martensite compared to austenite [50, 300]. Moreover, prestraining results in residual stresses which might reduce

the hydrogen solubility as well and adds to the total reduction of the hydrogen concentration after prestraining.

Thermal desorption spectroscopy was used to evaluate the average hydrogen diffusion coefficient as diffusion is the rate-determining step for the desorption of hydrogen in FCC steels (cf. Chapter 4). Deformation-induced features such as dislocations and vacancies are stated not to influence the hydrogen diffusivity of austenite since they are characterised by a low trapping activation energy compared to the diffusion activation energy of austenite [136, 148, 300, 301]. The specimen thickness was 0.3 mm. The thickness was reduced with respect to the melt specimens to enlarge the fraction of material that was charged with hydrogen given that the heterogeneous hydrogen concentration profile determines the appearance of the desorption spectrum for low-hydrogen diffusivity materials. As such, the peak that represents diffusion through the uncharged bulk of the specimen is less extended over a broad temperature range and thus more clearly distinguishable from the background signal. Figure 6-5 shows a plot of the tests performed at a heating rate of 600 K/h and 900 K/h for both as-received and prestrained 304L ASS. All spectra consisted of two peaks, one main peak and a high temperature shoulder. The first peak can be understood as hydrogen that diffused out of the specimen towards the nearest surface while the second peak can be understood as hydrogen that left the specimen via diffusion through the uncharged sample centre and then to the sample surface driven by the lower chemical potential at these locations [208]. The peak splitting is thus a direct result of the heterogeneous hydrogen concentration, as demonstrated in chapter 4. Comparison of the spectra of both materials at the same heating rate, indicated a small shift in peak position of the two peaks. The first peak maximum shifted to a higher temperature while the second peak maximum shifted to a lower temperature as illustrated in Figure 6-5. Both shifts are an indication that hydrogen diffused further into the specimen during charging in the case of prestrained 304L ASS. For the first peak, a higher peak maximum represents a larger diffusion distance. For the second peak, hydrogen that diffused deeper into the material and/or is characterised by a faster average hydrogen diffusivity leads to a reduction of the diffusion time to the opposite surface. Diffusion was thus slightly faster in the prestrained material. Mine et al. [164] similarly performed TDS measurements on severely plastically deformed 304 ASS and stated that hydrogen desorption was controlled by diffusion. Their spectra contained one peak and the peak temperature shifted to lower values with increasing prestrain. Given that the materials were homogeneously charged by gaseous hydrogen charging, hydrogen diffusion was thus indeed enhanced by the presence of the martensite phase. A similar conclusion was made based on the effective hydrogen diffusion coefficients reported in Table 6-1 determined by gaseous hydrogen permeation experiments.



Figure 6-5: Thermal desorption spectroscopy data of as-received and prestrained 304L ASS charged for seven days at room temperature

In chapter 4, a model was constructed to reproduce TDS spectra based on Fick's laws for diffusion. This model was used to simulate the tests that were performed in the present work as well. Both the charging and discharging process were simulated with the appropriate boundary conditions as given in Chapter 4. The initial concentration before charging was assumed to be zero. The output of the charging simulation was used as initial condition for the discharging simulation. The boundary condition for charging was Cs at the edges while a zero boundary condition was applied for discharging. Charging occurred at a constant temperature while discharging was modelled with a constantly increasing temperature via the heating rate. The model was, however, unable to fit the mean peak and the shoulder at the same time. Intuitively, the most suitable way to obtain the effective hydrogen diffusivity of a material is by fitting the high temperature shoulder since the second peak results from diffusion through the bulk while the first peak might be prone to surface effects. A first indication of the presence of surface effects is the small increase in hydrogen flux just after the start of the measurement for some conditions (most pronounced for asreceived 900 K/h in Figure 6-5). A skin effect has been reported after electrochemical hydrogen charging referring to a supersaturated hydrogen concentration in the first few atomic layers of a material [302]. Moreover, since slip lines were clearly observed on the surface (cf. Figure 6-4), the effective hydrogen diffusivity might be altered compared to the bulk value. The latter is considered less of an issue for hydrogen that diffused first towards the uncharged bulk since this diffusion step will be the controlling factor in the desorption speed. The resulting least square fits for both heating rates based only on the experimental data above 200°C are presented in Figure 6-6 and Figure 6-7. The obtained fitting parameters are given in Table 6-3.  $C_s$  represents the hydrogen surface concentration,  $D_0$  the preexponential factor and Q the activation energy of the effective diffusivity. At room temperature, both materials show a diffusivity in the range of 1E-16 m<sup>2</sup>/s to 2E-16 m<sup>2</sup>/s. The found value is in close agreement with the values reported in Table 6-1 when evaluated at room temperature. The slightly different temperature dependency might be related to the higher temperature range in which the authors determined their equations, i.e. through high temperature gaseous hydrogen permeation. In the work of Perng and Altstetter [71], the D<sub>0</sub> and Q value were also shown to depend on the temperature range for 301 ASS with different amounts of deformation. A lower temperature range resulted in a higher D<sub>0</sub> and Q value. The hydrogen solubility is in agreement with chapter 4 where a 50/50 austenite/ferrite duplex stainless steel had an equilibrium surface concentration of about 700 wppm using the same electrolyte and charging conditions. Omura et al. [303] also reported similar surface hydrogen concentration values for various stainless steels after electrochemical hydrogen charging using comparable conditions. The clear resemblance with literature data based on the fit of the high temperature shoulder additionally indicates that the first peak is indeed influenced by a surface effect, i.e. hydrogen leaves the specimen more readily than what can be expected from its bulk hydrogen diffusivity.

	C <sub>s</sub> [wppm]	D₀ [m²/s]	Q [kJ/mol]
As-received 304L	1510	2.76E-6	58.23
Prestrained 304L	1303	2.75E-6	57.94

Table 6-3: Fitting parameters of the diffusion fit to the experimental TDS data



Figure 6-6: Diffusion fit based on Fick's laws to the experimental TDS data of as-received 304L ASS, the fitting procedure focused on the data above 200°C



Figure 6-7: Diffusion fit based on Fick's laws to the experimental TDS data of prestrained 304L, the fitting procedure focused on the data above 200°C

Figure 6-8 shows the calculated hydrogen concentration profile after the performed pre-charging procedure at room temperature (295K) for as-received and prestrained 304L ASS. It is clear that only a small region (approximately 35 µm) near the surface showed an enlarged hydrogen concentration after pre-charging. It should be noted that the difference in diffusivity between both material conditions is rather small as only a small percentage of martensite was formed and the martensite islands were not interconnected.



Figure 6-8: Hydrogen concentration profile for as-received and prestrained 304L ASS with parameters obtained from diffusion fit to TDS data
## 6.3. Influence of cold work on hydrogen solubility and diffusivity of 304 ASS evaluated after gaseous hydrogen charging<sup>10</sup>

An AISI 304 austenitic stainless steel was subjected to different amounts of cold rolling reduction to evaluate the influence of prior deformation on the hydrogen solubility and diffusivity in metastable austenitic stainless steels. The chemical composition of the steel used in this section can be found in Table 6-4 which differed slightly from the previously described 304L stainless steel. The as-received material was solution annealed at a temperature of 1180°C for three minutes. Subsequently, the material was cold rolled to four different thickness reductions: 15%, 30%, 45% and 60%. Cylindrical bars were machined from the center of the cold rolled plate, as illustrated in Figure 6-9 (a). The final dimensions of the specimens used for the hydrogen analysis can be found in Figure 6-9 (b).

Table 6-4: Chemical composition of AISI 304 ASS used for gaseous hydrogen charging



Figure 6-9: Illustration of the machining (a) and final specimen dimensions (b) for hydrogen testing of cold rolled 304 ASS

EBSD measurements were performed to visualise the cold rolled microstructure. A cross-section of the cylindrical specimens along the rolling direction was prepared. A representative measurement for the four material conditions is shown in Figure 6-10. Both an image quality and phase map are shown. The higher the amount of cold rolling, the more points are measured with a low confidence index which is a direct result of the applied strain. An increasing martensite fraction with cold rolling reduction is clearly observed in the images. The a'-martensite fraction is present as separate islands for the low cold rolling reductions, however, at 60% thickness reduction, larger interconnected zones are present that could serve as hydrogen diffusion paths.

<sup>&</sup>lt;sup>10</sup> The present work was performed in collaboration with Kyushu University, Japan where gaseous hydrogen charging was executed. Analysis of the obtained data was performed at Ghent University in the framework of this PhD



Figure 6-10: Image quality and phase maps as determined through EBSD of the four different cold rolled 304 ASS (a,b) 15%, (c,d) 30% , (e,f) 45% and (g,h) 60% cold rolling reduction

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Feritscope measurements were performed on the different cold rolled materials to evaluate the fraction of strain-induced a'-martensite. The circular section of Figure 6-9 (b) was subjected to the measurements, i.e. the RD plane. The results can be found in Figure 6-11. As expected, the a'-martensite fraction increased with the amount of reduction by cold rolling, i.e. with increasing amounts of plastic strain. Wasnik et al. [304] found similar a'-martensite fractions as a function of the cold rolling reduction for 304 ASS. The a'-martensite fraction typically shows a sigmoidal increase as a function of the amount of plastic strain [305].



Figure 6-11: a'-martensite fraction as a function of the cold rolling reduction as determined with Feritscope measurements

Gaseous hydrogen charging was performed in an autoclave at a pressure of 100 MPa and a temperature of 300°C. Hydrogen diffusion was modelled with Fick's second law in cylindrical coordinates (r, $\theta$ ,z) to evaluate whether the specimens contained a homogeneous hydrogen concentration after a charging time of 66 hours (procedure applied at Kyushu University). The  $\theta$  dependency was neglected. The resulting differential equation is:

$$\frac{\partial C}{\partial t}(r, z, t) = D\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) + \frac{\partial^2 C}{\partial z^2}\right)$$
(6-1)

The initial hydrogen concentration was zero throughout the entire cylindrical specimen. At the start of the charging procedure, a normalised hydrogen concentration of one was applied to the three outer surfaces as boundary condition:

$$C(X,z,t) = 1; C(r,1,t)=1 \text{ and } C(r,Z,t)=1 \text{ for } t>0$$
 (6-2)

With X the radius of the cylindrical specimen (2.5 mm) and Z the height of the specimen (1 mm). The time discretisation was chosen based on the Von Neumann stability criterion:

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dt = 
$$0.2 * \frac{\frac{1}{2} * \min(dr^2; dz^2)}{D}$$
 with a maximum value of 1 s (6-3)

The effective hydrogen diffusivity at 300°C was evaluated based on the temperature dependent equation determined for as-received 304 austenitic stainless steels by Xiukui et al. [294]. Since the diffusivity is expected to be higher for the material conditions tested in the present work due to the transformation to a'-martensite, a homogeneous hydrogen concentration will most likely be reached earlier in the studied cold rolled materials.



Figure 6-12: Simulation of the charging profile during gaseous hydrogen charging at 300°C for 304 ASS with a cylindrical geometry as given in Figure 6-9 (b). Hydrogen diffusivity data from [294]

The average hydrogen concentration in the four cold rolled 304 ASS after the constant gaseous charging procedure is given in Figure 6-13. The hydrogen solubility dropped with increasing cold rolling reduction. As the steels contained a homogeneous hydrogen concentration, this can be attributed to the lower hydrogen solubility of the a'-martensite phase. The electrochemical charging conditions used in section 6.2 were clearly more severe, cf. Table 6-3, as the equilibrium surface hydrogen concentration C<sub>s</sub> was much higher compared to the values determined after gaseous charging at 300°C and 100 MPa.



Figure 6-13: Homogeneous hydrogen concentration after gaseous charging at 300°C and 100 MPa for 66 hours for the four cold rolled 304 ASS

The homogeneously hydrogen precharged materials were subsequently analysed to determine the effective hydrogen diffusivity. In a first approach, the specimens were heated at a constant temperature. Hydrogen effusion was subsequently measured as a function of time. The hydrogen diffusion coefficient can be determined from the desorption curve by analytically solving Fick's second law with specific boundary conditions as illustrated by Yamabe et al. [306]. The hydrogen concentration C(t) left in the specimen as a function of desorption time t (>>0), can be expressed as [306]:

$$\frac{C(t)}{C_{\rm S}} \approx \frac{32}{\pi^2 \beta_1^2} \exp\left[-\left(\frac{\pi^2}{z_0^2} + \frac{\beta_1^2}{r_0^2}\right) {\rm Dt}\right]$$
(6-4)

In this equation, C<sub>s</sub> is the equilibrium surface hydrogen concentration [wppm], β<sub>1</sub> is the first root of the zero order Bessel function (2.405), z<sub>0</sub> is the specimen height [m], r<sub>0</sub> is the specimen radius [m] and D is the diffusion coefficient at the constant test temperature. To be able to conduct this type of analysis, specimens should be homogeneously charged with hydrogen. Since this was not possible using the electrochemical charging procedure in a reasonable amount of time, gaseous charging provided a good alternative.

Hydrogen effusion experiments were performed at four different constant temperatures in order to evaluate the dependence of the hydrogen diffusion coefficient on the temperature as well. The hydrogen flux leaving the specimen was detected with a mass spectrometer. The used temperatures were 150°C, 200°C, 250°C and 300°C. Figure 6-14 shows the desorption curves for the 60% cold rolled 304 ASS. The lower the temperature, the longer the time needed for hydrogen to desorb due to the lower hydrogen diffusivity. By fitting equation (6-4) to the experimental curves, the diffusion coefficient was determined for every condition. The result of this analysis can be found in Figure 6-15. The diffusion coefficient clearly

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increased with the amount of cold rolling. Table 6-5 summarises the effective hydrogen diffusion coefficients as determined from the linear trend in Figure 6-15. The higher diffusivity of the a'-martensite phase could explain an increase in the effective hydrogen diffusivity.



Figure 6-14: Hydrogen desorption profile at different constant temperatures for gaseous hydrogen charged 304 ASS with 60% cold rolling reduction





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	$D_0 [m^2/s]$	Q [kJ/mol]	
15% CR	3.2E-7	45.3	
30% CR	2.5E-7	43.3	
45% CR	1.6E-7	39.6	
60% CR	3.5E-7	39.1	

Table 6-5: Hydrogen diffusion coefficient determined from the linear trend in Figure 6-15

In a second approach, thermal desorption spectroscopy data were analysed and fitted with the numerical diffusion model in cylindrical coordinates (cf. the procedure in section 4.4). It was assumed that the materials contained a homogeneous hydrogen concentration before the TDS experiment, as this could be confirmed based on Figure 6-12. At the start of the TDS test, a zero hydrogen concentration was applied to the three outer surfaces as boundary condition:

$$C(X,z,t) = 0; C(r,1,t)=0 \text{ and } C(r,Z,t)=0 \text{ for } t>0$$
 (6-5)

With X the radius of the cylindrical specimen (2.5 mm) and Z the height of the specimen (1 mm).

Figure 6-16, shows the experimentally obtained TDS data using a heating rate of 600 K/h. All materials showed a similar shape characteristic for a homogeneously hydrogen charged material with low hydrogen diffusivity. The result of the fitting procedure can be found in Figure 6-17. Table 6-6 summarises the obtained values for the pre-exponential factor D<sub>0</sub> and the diffusion activation energy Q. The values are in close agreement with the ones reported in Table 6-5. Figure 6-18 gives a visual representation of the effective hydrogen diffusion coefficients determined by both methods (M1 = constant temperature desorption experiments and M2 = numerical fit of thermal desorption spectroscopy data). Values found in literature that were reported in Table 6-1 were added to the graph as well. The a'-martensite fractions that were measured in the different materials were added to the legend. At room temperature, the increase in diffusivity is similar for 30% to 45% and 45% to 60% cold rolling reduction. The difference between 15% and 30% is, however, more limited. At a certain martensite fraction, the a'-martensite islands might be more interconnected as such altering the diffusivity more significantly, i.e. the creation of a fast hydrogen diffusion path.

The TDS-based method systematically resulted in a slightly higher hydrogen diffusivity for the four materials tested. The difference between both methods could be attributed to the approximations that were made to obtain equation (6-4), discrepancies between the applied and true heating rate and experimental errors. Yamabe et al. [306] have shown that equation (6-4) could underestimate the hydrogen diffusivity since additional terms were neglegted because of the assumed large desorption time. Secondly, for TDS tests, the true heating rate is often a little lower than the applied heating rate. This applied heating rate was, however, used in the numerical fitting procedure. The use of a slightly higher heating rate leads to a small overestimation of the hydrogen diffusion coefficient which is consistent with the observations in Figure 6-18.

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Comparison with literature data indicates that the slope of the linear trend in Figure 6-18 can vary significantly although the order of magnitude for the hydrogen diffusivity is still comparable. The temperature validity range for the obtained expression might be an important factor to explain this difference. Moreover, the surface oxide layer might be different after the divergent charging methods that are used in literature. This surface oxide layer could affect the desorption speed of hydrogen, although diffusion is also low in the austenite matrix meaning that it is unlikely that diffusion through the oxide layer would be the rate determining step.



Figure 6-16: Thermal desorption spectroscopy data tested at a heating rate of 600 K/h for cold rolled 304 ASS to different thickness reductions



Figure 6-17: Numerical diffusion fit of the thermal desorption spectroscopy data at 600 K/h for 304 ASS cold rolled to different thickness reductions

# Table 6-6: Hydrogen diffusion coefficient determined from numerical diffusion modelling of experimental

D <sub>0</sub> [m²/s]		Q [kJ/mol]	
15% CR	3.6E-7	44.7	
30% CR	3.4E-7	42.8	
45% CR	2.5E-7	39.5	
60% CR	2.7E-7	37.1	



Figure 6-18: Average hydrogen diffusivity as a function of temperature for four cold deformed 304 ASS determined via two methods (M1 = constant temperature hydrogen desorption, M2 = TDS), literature data was included as well (Perng et al. [71] and Xiukui et al. [294]), the percentage of a'-martensite is given in the legend

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## 6.4. <u>Conclusions</u>

Electrochemical hydrogen charging of 304L ASS at room temperature was successfully performed in the present work. The following conclusions were drawn:

- Slip bands were formed on the specimen surface. However, no martensitic transformations occurred due to the charging procedure.
- Numerical diffusion modelling enabled the determination of the hydrogen diffusivity and surface hydrogen concentration based on thermal desorption spectroscopy data. The effective hydrogen diffusion coefficient for both the as-received and 30% tensile prestrained 304L stainless steel at room temperature was in the order of 1-2E-16 m<sup>2</sup>/s, i.e. tensile prestraining did not alter the hydrogen diffusivity significantly.
- Both materials showed a hydrogen penetration depth of approximately 35 µm after seven days of precharging, i.e. a heterogeneous hydrogen distribution was reached.

The possibilities of gaseous hydrogen charging were explored for 304 ASS cold rolled to different thickness reductions (15%, 30%, 45% and 60%) in collaboration with Kyushu University (Japan):

- A homogeneous hydrogen concentration was reached for all material conditions.
- The total hydrogen concentration in the specimens clearly dropped with increasing cold deformation due to the presence of a'-martensite with a lower hydrogen solubility.
- The hydrogen diffusivity was evaluated using two different approaches. First, constant temperature hydrogen desorption tests were fitted by an approximated analytical solution of Fick's second diffusion law. Secondly, numerical diffusion modelling of thermal desorption spectroscopy data was used. Both methods resulted in comparable results for the temperature dependency of the effective hydrogen diffusion coefficient which were consistent with literature data as well.

# Chapter 7 Hydrogen-induced mechanical degradation and the effect of crosshead displacement rate in 304L austenitic stainless steel<sup>11</sup>

## 7.1. Introduction

Austenitic stainless steels exhibit excellent mechanical properties. Despite a relatively low yield strength, AISI 304L ASS shows a lot of strain hardening reaching high ultimate tensile strengths. The high formability while maintaining a high strength is a result of the transformation induced plasticity (TRIP) effect, i.e. the metastable austenite ( $\gamma$ ) transforms to epsilon ( $\epsilon$ ) martensite and/or alpha prime ( $\alpha$ ') martensite under the application of strain [307, 308].  $\epsilon$ -martensite nucleates due to the overlap of stacking faults on every second {111} plane. Strain-induced  $\alpha$ '-martensite is stated to nucleate at various possible locations. These include shear band intersections, isolated shear bands, shear band/grain boundary intersections and grain boundary triple junctions [309]. Kaoumi et al. [310] used in-situ TEM observation to study the deformation induced martensite transformation in AISI 304 ASS and confirmed the possibility of three different transformation routes, i.e.  $\gamma \rightarrow \epsilon$ ,  $\gamma \rightarrow \epsilon \rightarrow \alpha'$  and  $\gamma \rightarrow \alpha'$ . Regarding the latter transformation route, these authors found that the interface migrated upon pulling of the specimen and stopped when the stage was at rest. The transformation was thus a direct result of the applied strain. At room temperature, the transformation to  $\alpha'$ -martensite dominates for 304L ASS [297].

The applied strain rate during tensile testing has been stated to influence the strain-induced martensitic transformations. According to Olson and Cohen [311], the martensite content decreases with decreasing strain rate as less of the previously mentioned nucleation sites are formed. Buckley et al. [262] indicated that the martensite fraction did not vary significantly for strain rates ranging from 2E-6 to 2E-3E-3 s<sup>-1</sup>. The inherent strain rate sensitivity of 304 ASS was thus found to be limited [312]. However, plastic deformation gives rise to adiabatic heating, which is much more pronounced at fast strain rates due to the limited time for the heat to dissipate into the surroundings. As a result, the amount of martensite and therefore also the strength and ductility, is usually reduced at high strain rates [313].

Brass et al. [314] investigated the influence of the applied strain rate on the hydrogen embrittlement sensitivity of cathodically precharged 304L ASS. The authors illustrated clearly that the susceptibility to hydrogen decreased with increasing strain rate. Buckley et al. [262] also found an increase in HE with decreasing strain rate for 304L ASS until a maximum was reached and the HE decreased again with

<sup>&</sup>lt;sup>11</sup> This chapter was based on the following publication: L. Claeys, I. De Graeve, T. Depover and K. Verbeken, "Impact of hydrogen and crosshead displacement rate on the martensitic transformations and mechanical properties of 304L stainless steel", Theoretical and applied fracture mechanics 113 (2021), 102952, https://doi.org/10.1016/j.tafmec.2021.102952

decreasing strain rate. As the authors performed ex-situ tensile tests with precharged hydrogen, a lot of hydrogen desorbed from the specimen at the low strain rates explaining the drop in HE sensitivity. Pan et al. [315] also confirmed the increasing HE sensitivity (based on the elongation at fracture) with decreasing strain rate and determined a logarithmic equation for the strain rate dependency for 304L stainless steel: %HE = -3.6 - 4.3\*LN(strain rate).

Metastable austenitic stainless steels were found to be more prone to HE compared to stable austenitic stainless steels, although austenite stability was stated not to be a sufficient criterion for the HE susceptibility of austenitic steels [133]. Briant [134] reported that the most detrimental effect on the HE susceptibility of AISI 304 ASS was the formation of strain-induced a'-martensite upon deformation, especially when it was formed along grain boundaries. Han et al. [135] similarly reported that HE occurred due to strain-induced o'-martensite presence along grain boundaries in sensitized austenitic stainless steels. For cathodically hydrogen charged specimens, Wang et al. [316] showed that the HE sensitivity increased largely with increasing prestrain level. A direct relation with the a'-martensite fraction was found. 304L ASS prestrained at 50 and 80°C exhibited less HE due to the lower a'-martensite fraction after prestraining [136]. The HE sensitivity at 80°C of non prestrained 304L ASS was also lower than the HE during straining at 25°C due to suppressed formation of a'-martensite [317]. Hydrogen-induced slow crack growth did even not occur when 304 ASS was tensile tested in gaseous hydrogen atmosphere above the  $M_d$ -temperature, i.e. the temperature above which no strain-induced martensitic transformations take place [318]. Perng et al. [319] observed a high crack growth rate in 301 ASS due to the presence of a'martensite at the crack tip. Martin et al. [320] observed that machining-induced o'-martensite at the surface of 304 ASS was detrimental for its HE resistivity. In all of the above cases, the reason for the observed increased HE sensitivity with increasing a'-martensite fraction is the large difference in hydrogen solubility and diffusivity compared to the parent austenite phase [321]. Buckley et al. [262] observed, however, that prestraining reduced the HE sensitivity and was independent of the amount of straininduced a'-martensite. The produced dislocation substructures were thought to be responsible for the observed decreasing trend with prestrain level. Zhang et al. [138] stated that prior strain-induced a'martensite has little relation with HE while dynamic a'-martensite formed during a tensile test increased the HE sensitivity since dynamic o'-martensite is supersaturated with hydrogen upon transformation. Zhou et al. [322] stated that the type of embrittlement was important. HE increased with increasing prestrain level for internal hydrogen, while HE reached a maximum with increasing pre-stain level for external hydrogen. The latter was explained by the reduction in dislocation main free path limiting the possible hydrogen transport distance during the tensile test following prestraining.

Consequently, the interaction between hydrogen and deformation-induced martensite in 304L ASS is still under debate. The role of pre-existing a'-martensite on HE of 304L ASS will be evaluated in the presence of high hydrogen concentrations after cathodic hydrogen charging to validate the mentioned literature observations in the present work. Moreover, an in-depth study of the influence of hydrogen on the straininduced martensitic transformation will be performed through electron backscatter diffraction (EBSD), which has rarely been applied in the mentioned state-of-the-art literature works and can identify both  $\varepsilon$ and  $\alpha$ '-martensite [323, 182]. Finally, different constant crosshead displacement rates will be applied. This will allow to evaluate the influence of hydrogen diffusion on HE of 304L ASS and to analyse the influence of strain rate on martensitic transformation (adiabatic heating effect) in the presence of hydrogen.

#### 7.2. Influence of the crosshead displacement rate on the mechanical properties

The used materials in this section were introduced and characterised in section 6.2. The as-received and prestrained 304L ASS were tested at engineering strain rates of 3.3E-2, 1E-3 and 3.3E-5 s<sup>-1</sup>. The reference tests were performed in air. For the hydrogen condition, specimens were precharged for seven days and were subsequently tested in-situ. The results of the tests are presented in Figure 7-1 (a) for as-received 304L ASS and in Figure 7-1 (b) for prestrained 304L ASS. Both the reference tests performed in air and the in-situ hydrogen tests are reported. For every condition, the experiments were repeated three times to confirm the reproducibility of the tests, however, only one of the performed tests is shown. Table 7-1 illustrates the reproducibility of the results by showing the range of elongations at fracture at every test condition. It should be noted that the engineering strain was calculated based on the crosshead displacement. Since the strain was not measured directly due to the limitations of an environmental cell, the mentioned engineering strain rates are hence not exact but were calculated based on the constant displacement rates and the initial gauge dimensions.

The tests performed in air differed depending on the applied engineering strain rate. The faster the displacement rate, the higher the yield strength and the smaller the elongation at fracture were. Both the as-received and the prestrained 304L ASS showed this behaviour. The engineering stress-strain curves at an engineering strain rate of 1E-3 and 3.3E-5 s<sup>-1</sup> were comparable for both material conditions with respect to elongation and strength at fracture. Similar strain rates were used for as-received 304L in the work of Lichtenfeld et al. [324]. The authors also reported a similar tensile behaviour for strain rates in the order of 1E-3 s<sup>-1</sup> to 1E-5 s<sup>-1</sup>, while a reduced ultimate elongation was observed for a strain rate of 1.25E-2 s<sup>-1</sup>. Talyan et al. [312] similarly reported this difference for a strain rate of 1E-2 and 1E-3 s<sup>-1</sup>. The shape of their engineering stress-strain curves are also comparable to the present work. The ultimate elongation at fracture was lower (70% for 1E-3 s<sup>-1</sup> compared to 90% in the present work) which is a direct result of the different strain measurement. The authors calculated the strain based on extensometer results while the strain was calculated from the crosshead displacement in the present work. Das et al. [325] performed tensile tests on 304LN ASS and clearly indicated a constant ductility for strain rates of 1E-4 and 1E-3 s<sup>-1</sup> and a continuous drop in ductility for higher strain rates. The authors also reported a continuous increase of the yield strength with increasing strain rate. Li et al. [326] performed tensile tests at different strain rates in air on 304 ASS as well. The authors also mentioned that the yield stress continuously increased with increasing strain rate. At the initial stages of deformation, martensite formation is low [326]. Dislocation slip controls the initial increase in flow stress which is enhanced at higher strain rates and thus results in a higher yield strength. At higher strain levels, martensite formation plays a dominant role in the increase in flow stress and ductility [297]. Due to adiabatic heating, less martensite is formed at high strain rates. As a result of the restriction of martensitic transformations, a lower ductility is reached [309, 312, 324, 326, 327]. Prestraining of 304L ASS resulted in an increase in yield strength, a decrease in elongation at fracture and a decrease in work-hardening [328]. All deformation features, e.g. dislocations and martensite, that were formed during prestraining limited the ability to accommodate additional plastic deformation during tensile testing.



Figure 7-1: Engineering stress as a function of engineering strain for as-received (a) and prestrained (b) 304L ASS

Engineering	As-received 304L		Prestrained 304L		
strain rate [s <sup>-1</sup> ]	Air	Hydrogen	Air	Hydrogen	
3.3E-2	65.2-68.0	74.0-75.5	25.5-27.1	26.0-27.4	
1E-3	91.0-92.6	65.5-65.7	36.1-37.4	21.7-21.9	
3.3E-5	85.6-88.6	36.4-40.6	34.8-35.0	13.4-15.5	

Table 7-1: Range of measured elongations for the different test conditions illustrating the reproducibility of the results

Hydrogen had a large influence on the mechanical properties as illustrated by the dotted lines in Figure 7-1 (a) and (b). Based on the average elongation at fracture for the air and in-situ hydrogen tests, an average embrittlement index (EI) was calculated (cf. equation 3-2). The deviation (dev) on this value was calculated from the difference between the largest and smallest possible embrittlement index. As the elongation was calculated based on the crosshead displacement, the EI inherently contains an error and the values do not represent a true quantitative loss in ductility. This procedure is, however, frequently used for in-situ tested austenitic steels [315, 329]. Figure 7-2 shows the EI as a function of the engineering strain rate for the as-received and prestrained 304L ASS.



Figure 7-2: Embrittlement index as a function of strain rate for as-received and prestrained 304L ASS with air reference

The EI was strongly dependent on the applied strain rate for both materials. The slower the strain rate, the more sensitive both materials were to hydrogen. This is in agreement with previous observations in literature for 304 ASS [314, 262]. The values were comparable to what could be expected from the equation proposed by Pan et al. [315] at the lowest two strain rates. However, the authors performed different charging conditions compared to the present work such as precharging for 48h at 50 mA/cm<sup>2</sup> and testing

in air or in-situ hydrogen charging without precharging. A one on one comparison of the results is thus not possible. An explanation for the observed strain rate dependency can be found in the time that is given for hydrogen to diffuse through the microstructure and accumulate at stress concentrations. When fast strain rates are applied, the diffusion distance is very small and the ability of hydrogen to accumulate at a crack tip or stress concentration and as such embrittle the material is very limited. At slow strain rates, however, hydrogen diffusion is more substantial and leads to hydrogen accumulation at crack tips and subsequently hydrogen-assisted crack propagation. Hydrogen diffusion and the hydrogen concentration that can be reached as a result of diffusion at crack tips are thus determining parameters in the hydrogen embrittlement sensitivity of 304L ASS. The role of strain rate and hence hydrogen diffusion on the HE degree has been demonstrated for other materials as well and is accepted [330, 331]. The strain rate effect might be lower if the specimens were homogeneously charged with hydrogen throughout the entire thickness since concentration gradients have been eliminated then. Diffusion driven by stress gradients can, however, still occur when the material was initially homogeneously charged resulting in differences between the strain rates due to the time given for diffusion as well. The effect of strain rate was clearly illustrated for homogeneously hydrogen charged specimens by Buckley et al. [262].

The prestrained material had a higher EI for all tested strain rates which is consistent with most literature observations [138, 316, 320]. One reason might be a higher effective hydrogen diffusivity due to the formation of a'-martensite. As measured through TDS (cf. Figure 6-8), the difference in initial hydrogen diffusivity can, however, be regarded as insignificant in the present work. As stated in the introduction, Zhang et al. [138] also pointed out that the prior induced a'-martensite fraction has little relation with HE, especially when the fraction is low. Secondly, the pre-existing a'-martensite fraction located at the surface might provide hydrogen to the surrounding austenite matrix at a higher speed leading to crack initiation. Finite element studies have shown that it is definitely possible that the reason for HE in metastable ASS is related to the drastically increased hydrogen concentration in austenite that is located in the close neighbourhood of martensite islands [332]. Other deformation-induced features (e.g. dislocations) that were formed during prestraining might additionally have led to a higher embrittlement of the prestrained steel as the stress concentrations associated with for example dislocation pile-ups attract and accumulate hydrogen. With decreasing strain rate, the EI of the as-received and prestrained 304L ASS approached each other. The test time became less of a limiting factor when the strain rate was very low and the formation of large stress concentrations followed by hydrogen diffusion and accumulation was not limited anymore.

One remarkable observation deserves more attention. At a strain rate of 3.3E-2 s<sup>-1</sup>, the EI was negative for the as-received material, i.e. a higher elongation at fracture was observed in the hydrogen charged condition compared to the air test. As mentioned previously, at fast strain rates, adiabatic heating reduced the elongation at fracture due to restricted martensitic transformation. The surface temperature of the as-received 304L ASS reference test in air at a strain rate of 3.3E-2 s<sup>-1</sup> was measured with a K-type thermocouple point welded to the gauge section. A temperature increase of 20°C was measured at the

surface of the specimen during a short time interval as can be seen in Figure 7-3. The temperature increase might be higher in the bulk. In the work of Talyan et al. [312], the temperature increased with about 20°C as well for a strain rate of 1E-2 s<sup>-1</sup>. Moreover, alternative reference tensile tests were performed where the adiabatic heating effect was counteracted by a surrounding solution rather than air (in-situ cell with demineralized water) as well. The results for the as-received 304L ASS performed at 3.3E-2 s<sup>-1</sup> and 1E-3 s<sup>-1</sup> are given in Figure 7-4. At an engineering strain rate of 3.3E-2 s<sup>-1</sup>, the macroscopic tensile curve reached both a higher UTS and a higher elongation at fracture. Similar results for the reference test in air and in solution were, however, obtained at a strain rate of 1E-3 s<sup>-1</sup>. The adiabatic heating effect is thus only important for the fastest strain rate in the present work. Other authors reported similar threshold values (order of 1E-2 s<sup>-1</sup>) for the occurrence of an adiabatic heating effect as a function of strain rate for 304 ASS [324]. Talyan et al. [312] measured the temperature at a strain rate of 1E-3 s<sup>-1</sup> and observed a more or less constant temperature through time. Only at very high strains, the temperature increased quickly with about 10°C. The authors also illustrated the large increase in engineering strain that could be obtained by executing the tensile test in stirred water at room temperature at a strain rate of 1E-1 s<sup>-1</sup>. The embrittlement index was corrected with reference tests performed in solution for both materials and is given in Figure 7-5. It is clear that when the appropriate reference test is used, all conditions led to hydrogen reducing the elongation at fracture.



Figure 7-3: Temperature profile measured with a thermocouple during the air reference test on asreceived 304L ASS at 3.3E-2 s<sup>-1</sup>



Figure 7-4: Engineering stress-strain curves including reference tests in solution for as-received 304L ASS tested at 3.3E-2 and 1E-3 s<sup>-1</sup>



Figure 7-5: Embrittlement index as a function of strain rate for as-received and prestrained 304L ASS: solution reference instead of air reference (Figure 7-2)

#### 7.3. Influence of hydrogen on fracture and deformation

The fractured specimens were subsequently investigated with SEM. The fracture surface of the air tested specimens showed ductile dimples. No clear differences in dimple size and shape were observed for the different strain rates and for whether the 304L ASS was prestrained or not. Figure 7-6 (a) shows an example of dimples that were observed on the fracture surface (ND = normal direction) of as-received 304L ASS tested at 1E-3 s<sup>-1</sup>. The specimens tested with hydrogen showed similar dimples in the center of the fracture surface. The edges were, however, clearly embrittled by hydrogen. For 304 ASS, the type of brittle fracture is stated to depend on the amount of hydrogen in [333]. The fracture surface changes from quasi-cleavage to intergranular fracture. In the present work, quasi-cleavage fracture was observed which is consistent with the used current densities in [333]. An example is shown in Figure 7-6 (b) for prestrained 304L ASS tested at a strain rate of 1E-3 s<sup>-1</sup>. The presence of an embrittled zone near the surface can be interpreted as the location where hydrogen was present in sufficient amounts to alter the fracture behaviour. Since the hydrogen concentration was most likely not changed significantly in the center of the specimen during the tensile tests due to diffusion, the fracture surface remained unaffected there.





Depending on the applied strain rate, the size of the embrittled zone was different. The determined sizes are given in Table 7-2. The size of the brittle zone clearly increased with decreasing strain rate. The hydrogen precharging time was, however, equal for all tests, i.e. the distance hydrogen diffused before the start of the tensile test was equal for all as-received specimens on the one hand and for all prestrained specimens on the other hand (both approximately 35 µm, cf. Figure 6-8). However, decreasing the strain rate results in more time for hydrogen to diffuse during the in-situ tensile test and as a result a larger hydrogen embrittled zone. Moreover, as the test is ongoing, more a'-martensite is formed which continuously increases the average hydrogen diffusion coefficient of the material during the course of the

experiment. As such, hydrogen can reach deeper into the specimen than expected from the average diffusion coefficient of the materials before the start of the tensile test within the given test durations (see Table 7-2, approximate test duration). The brittle zones of the prestrained material were slightly larger than the ones of the as-received 304L ASS. The difference was, however, small which is in agreement with the analysis of the TDS data in Figure 6-8.

Table 7-2: Size of the brittle quasi-cleavage zone on hydrogen-tested specimens depending on the strain rate for as received and 30% prestrained 304L ASS, the average tensile test duration with in-situ hydrogen charging was added as well

Engineering	Thickness quasi-cleavage zone [µm]		Approximate test duration (min)		
strain rate [s <sup>-1</sup> ]	As-received	Prestrained	As-received	Prestrained	
3.3E-2	23-26	24-28	0.38 ± 0.003	0.13 ± 0.003	
1E-3	42-49	40-50	10.93 ± 0.02	3.63 ± 0.02	
3.3E-5	120-130	128-134	194.57 ± 10.53	72.95 ± 5.13	

A further in depth analysis of the variable hydrogen diffusion coefficient as a function of increasing strain was performed to be able to substantiate the observed brittle zones. Olson and Cohen [305] developed a model that describes the evolution of the a'-martensite fraction  $f_{\sigma}$  as a function of the equivalent plastic strain  $\varepsilon$ :

$$f_{\alpha'} = 1 - \exp\{-\beta[1 - \exp(-\alpha\epsilon)]^n\}$$
(7-1)

For deformation of 304L ASS at room temperature, the parameters n,  $\beta$  and a were fitted by the authors as 4.5, 3.55 and 0.5, respectively. The fitting ability of this type of equation is fairly good, however, the saturation volume fraction is for example not considered. Different modifications were done to the model [334], however, a discussion on the most appropriate model lies out of the scope of this work. The dependency of the hydrogen diffusion coefficient on the a'-martensite fraction in 304L was investigated by several authors as well. In general, the natural logarithm of the diffusion coefficient was found to scale with the natural logarithm of  $f_{a'}/(1-f_{a'})$  [71]. Wang et al. [316] proposed the following expression for the effective hydrogen diffusion coefficient D [m<sup>2</sup>/s] in 304L ASS valid for  $f_{a'} > 0.02$ :

$$\ln(D) = 0.811 \ln\left(\frac{f_{\alpha'}}{1 - f_{\alpha'}}\right) - 31.653$$
(7-2)

Combining both equations, yields the effective hydrogen diffusivity as a function of plastic strain  $\varepsilon$  for 304L ASS. Figure 7-7 shows the evolution based on the provided literature data. A value of about 1E-14 m<sup>2</sup>/s was found for an a'-martensite fraction of 36% which agrees with literature data on duplex stainless steels with 50% ferrite and an effective diffusion coefficient of 2.2E-14 m<sup>2</sup>/s to 6.4E-14 m<sup>2</sup>/s [72, 224, 225, 226]. The diffusion depth during the tensile test was subsequently evaluated using both equations. The evolution of the amount of plastic strain was related to the test time through the deformation rate and initial gauge length. Figure 7-8 shows the result of this analysis. The difference in diffusion depth between

the deformation rates clearly reflects the differences that were observed in the size of the brittle zone in Table 7-2. The used model was found to underestimate the actual size of the brittle zone, especially for the slow deformation rates if one additionally takes into account that a critical hydrogen concentration is needed before the fracture appearance is altered. This difference can be related to the use of the simplified models for both the variation of the fraction of a'-martensite with strain and the hydrogen diffusivity with the a'-martensite fraction, the inaccurate determination of the plastic strain which was thus also not correctly implemented in the model to evaluate the a'-martensite fraction, the presence of elastic stress during the tensile test which increases the hydrogen diffusivity, the absorption and accumulation of hydrogen directly at the crack tip from the surrounding atmosphere increasing crack growth and the enhanced hydrogen diffusion via dislocation motion during plastic deformation of austenitic steels [129]. Despite the lower test times for the prestrained 304L ASS, the brittle zone was almost identical in size (cf. Table 7-2). The effective hydrogen diffusivity most likely evolved faster with plastic strain compared to the as-received 304L ASS which makes sense as the initial a'-martensite fraction as well as many other a'martensite embryos formed by prestraining could lead to faster transformation kinetics [335].



Figure 7-7: Evolution of the effective hydrogen diffusion coefficient with increasing plastic strain due to an increase of the a'-martensite fraction:



Figure 7-8: Simplified model to estimate the hydrogen diffusion depth during the tensile tests at different deformation rates for as-received 304L ASS

The normal surface of the fractured specimens showed a lot of deformation when tested in air, as can be seen in the SE image of Figure 7-9 (a). The hydrogen charged specimens showed deformation as well, however, to a lesser extent. Moreover, they additionally showed many secondary cracks on the normal surface oriented perpendicular to the loading direction. Examples can be found in Figure 7-9 (b), (c) and (d) for different test conditions (the loading direction was parallel to the rolling direction). Hydrogenassisted crack (HAC) formation is generally observed when metals are strained under the presence of hydrogen. In austenitic steels, HACs are initiated at extreme slip localizations where the difficulty to crossslip induces large stress concentrations [151]. Secondly, HACs initiate at the interface of dynamic a'martensite islands. Hydrogen diffuses out of the supersaturated transformed o'-martensite to the interface with the austenite matrix where it causes crack initiation [139]. As-received 304L ASS tested at engineering strain rates equal to or higher than 1E-3 s<sup>-1</sup> showed large cracks over the entire section, cf. Figure 7-9 (b). The other specimens, i.e. as-received 304L ASS tested at 3.3E-5 s-1 and all prestrained specimens, showed small cracks over the entire section that were not visible at the magnification of Figure 7-9 (c) and (d). Large, developed cracks were only observed near the fracture surface, i.e. in the zones where the highest strains were reached. The tests that showed the least developed HACs over the entire section reached the lowest elongation at fracture and thus the lowest uniform strains. Only the region that was subjected to necking (and thus high strains) showed large cracks. It should be noted that crack initiation occurred early in the experiment for every material condition and engineering strain rate tested as a result of the high precharged hydrogen concentration over the entire gauge section. Recently, it was reported that subcritical cracking could impact the validity of the used ductility metric (EI) [336]. Materials that showed a superior performance with hydrogen based on this metric showed similar crack initiation times compared to more HE susceptible materials. The interpretation of slow strain rate tensile tests is thus not always unambiguous. For more reliable comparison of the ductility metrics, additional studies

are required with an adapted tensile test methodology, i.e. where fracture immediately follows crack initiation.

EBSD was subsequently used to study the deformed microstructure. Figure 7-10 shows an EBSD measurement on the normal plane of as-received 304L ASS tested in air at 3.3E-2 s<sup>-1</sup> and stopped at an intermediate elongation of 30%. The figure clearly indicates that the microstructure was deformed. Several islands of o'-martensite were formed. Deformation at room temperature predominantly initiated the direct y $\rightarrow$ a' transformation in 304 ASS [297]. Figure 7-11 shows an EBSD measurement on the normal plane of as-received 304L ASS that was tested with hydrogen at a strain rate of 3.3E-2 s<sup>-1</sup>. The test was also interrupted at an elongation of 30%. The black zones are HACs which were extracted from the measurement based on their low image quality. Comparison of Figure 7-10 and Figure 7-11 indicates that the deformation process changed significantly under the influence of hydrogen. Increased planar deformation [113] is clearly observable from the image quality map (central image of Figure 7-11) as many grains showed a lot of straight parallel lines. Since dislocation slip along the {111} planes is heavily promoted, the nucleation and growth of a'-martensite will also be more planar as the dislocation pile-ups and slip band intersections serving as o'-martensite embryos are formed within these planes and grow by addition of more dislocations to the pile-up or intersecting slip bands [41]. Increased planarity in the o'martensite fraction was also clearly observed in Figure 7-11. Moreover, an additional martensitic transformation route was initiated, i.e.  $y \rightarrow \epsilon \rightarrow a'$ . This transformation route is typically observed upon transformation of 304L ASS at cryogenic temperatures and is a result of a reduced stacking fault energy (SFE) [337]. This is consistent with previous studies indicating that hydrogen reduced the SFE of FCC steels [153, 154]. As ε-martensite is essentially formed by overlap of intrinsic stacking faults (formed between two partial dislocations) on every second {111} plane, the nucleation and growth of *ε*-martensite also has a planar appearance [41].



Figure 7-9: SE images of normal surface of fractured 304L ASS (a) as-received, air, 3.3E-2 s<sup>-1</sup>, (b) asreceived, H, 3.3E-2 s<sup>-1</sup> (c) as-received, H, 3.3E-5 s<sup>-1</sup> and (d) prestrained, H, 1E-3 s<sup>-1</sup>



Figure 7-10: EBSD measurement on ND surface of as-received 304L ASS tested in air at a strain rate of 3.3E-2 s<sup>-1</sup> stopped at an intermediate elongation of 30%



Figure 7-11: EBSD measurement on ND surface of as-received 304L ASS tested in-situ at a strain rate of 3.3E-2 s<sup>-1</sup> stopped at an intermediate elongation of 30%, cracks in black

The EBSD measurements indicated that the tests performed with hydrogen showed enhanced martensitic transformations (cf. Figure 7-10 and Figure 7-11). A more quantitative study was performed to have an idea on the extent of the martensitic transformations. For this purpose, the martensite fractions were measured by EBSD on the ND plane of specimens tensile tested and stopped at an intermediate elongation of 30%. The reference tests were performed in air for this study. The evolution of the formed martensite fraction as a function of increasing elongation was additionally studied by comparing the 30% elongation data to data of specimens stopped at an intermediate elongation of 60%. Moreover, the center of the TD plane was investigated for the specimens tested at a strain rate of 3.3E-2 s<sup>-1</sup> as well since hydrogen is expected not to be present there and therefore should not have influenced the martensitic transformations. As the crystallographic orientation with respect to the loading direction should be favourable to have martensitic transformation in individual grains, more than 100 grains were measured within a statistically relevant, constant scan area. The martensite area fractions are reported in Table 7-3.

The martensite fractions measured in air are in reasonable agreement with literature data. Similar fractions were reported in the work of Olson and Cohen [305]. Talyan et al. [312] reported a'-martensite fractions slightly lower than 10% for an intermediate strain of 30%. Taking into account the different strain measurements, this is in agreement with the present work as well. From the tensile tests, it was concluded that the air test at 3.3E-2 s<sup>-1</sup> was prone to an adiabatic heating effect, cf. Figure 7-4 (a). The martensite fraction on the ND plane at an elongation of 60% for a strain rate of 1E-3 s<sup>-1</sup> was clearly higher than for the strain rate of 3.3E-2 s<sup>-1</sup>. The difference was not yet visible at an elongation of 30% in the present work which is most likely due to the martensitic transformations being more active at higher strains and the higher temperature at higher strains. Table 7-3 indicates a slightly higher martensite fraction in the center of the hydrogen charged specimen (due to limited diffusion, no influence of hydrogen is expected there)

compared to the center of the reference test specimen in air at an intermediate elongation of 60% for an engineering strain rate of 3.3E-2 s<sup>-1</sup>. Talyan et al. [312] also observed a higher martensite fraction when testing was performed in stirred water compared to air. The bulk and surface martensite fractions in air are similar which is in agreement with literature works as well [324].

The martensitic transformation was enhanced at the surface of the hydrogen charged specimens compared to the air reference test (see Table 7-3, ND) for every tested strain rate and intermediate elongation. The g'-martensite fraction clearly increased in the presence of hydrogen. Moreover, an additional fraction of  $\varepsilon$ -martensite was detected, as already indicated qualitatively in Figure 7-11. The  $\varepsilon$ martensite fraction on the ND surface of 30% versus 60% elongation with hydrogen remained more or less constant. This might indicate that  $\epsilon$ -martensite acted as an intermediate phase for the transformation to a'-martensite. The ɛ-martensite fractions were calculated by a 0.2 Cl threshold because visual inspection confirmed that not all erroneous points were excluded by the 0.1 CI threshold. The hydrogen-enhanced martensitic transformation can be explained within the defactant concept as proposed by Kirchheim [338, 339] stating that adding solute atoms reduces defect formation energies as such increasing defect formation rates. In the present material, these defects include stacking faults, dislocations and interfaces between austenite and martensite. It should also be noted that the slip bands and other defects formed during the charging procedure could have served as nucleation sites for the martensitic transformation. The enhanced martensitic transformation is clearly more restricted for the fast strain rate (3.3E-2 s<sup>-1</sup>) compared to the other two tested strain rates which show similar martensite fractions. This is believed to be due to the limited test time. Hydrogen needs to be able to interact with dislocations to alter the martensite fractions which is more restricted at high deformation rates.

For the tests at a strain rate of  $3.3E-2 \text{ s}^{-1}$ , the enhanced martensitic transformation at the surface compared to the reference test in air might also be a result of the restricted adiabatic effect in solution. However, the enhancement of the transformation at all strain rates clearly indicates that hydrogen also contributed since no pronounced adiabatic effect was present for the tests at 1E-3 and  $3.3E-5 \text{ s}^{-1}$ . Moreover, it was demonstrated that hydrogen-induced martensitic transformations occurred in the austenite fraction of ex-situ tested duplex stainless steel, i.e. no solution effect was present in these tests (cf. Chapter 5). Finally, the presence of  $\varepsilon$ -martensite is a direct consequence of the high hydrogen concentration, since, although the adiabatic effect was restricted, the temperature was not actively decreased into a regime where  $\varepsilon$ martensite is favoured (cf. air tests). The enhanced  $\varepsilon$ - and  $\alpha$ -martensitic transformation at lower temperatures is a direct result of the reduced stacking fault energy and austenite stability with decreasing temperature, respectively [23, 318].

		Air		Hydrogen	
		a'-mart [%]	ε-mart [%]	a'-mart [%]	ε-mart [%]
Interrupted	ND (3.3E-2 s <sup>-1</sup> )	6.4	0.0	16.2	3.2
	ND (1E-3 s <sup>-1</sup> )	5.6	0.0	22.3	4.6
at 30%	ND (3.3E-5 s <sup>-1</sup> )	6.5	0.0	20.5	2.5
	TD (center) (3.3E-2 s <sup>-1</sup> )	6.9	0.0	8.2	0.0
Interrupted	ND (3.3E-2 s <sup>-1</sup> )	17.9	0.0	32.4	4.5
niterrupted	ND (1E-3 s <sup>-1</sup> )	23.9	0.0	48.3	3.7
dl 00%	TD (center) (3.3E-2 s <sup>-1</sup> )	20.8	0.0	25.6	0.0

Table 7-3: Martensite area fraction (%) measured with EBSD in different planes (ND and TD plane) at an intermediate elongation of 30% and 60%

Enhanced martensitic transformations should, simultaneously with the increase in elongation, be accompanied with an increase in strength level, as clearly observed when comparing the reference tests at 3.3E-2 s<sup>-1</sup> in air and in solution. However, the effective strength increase with hydrogen was rather limited. The formation of HACs on the normal surface might have an influence on the UTS. Especially at the faster strain rates (above 1E-3 s<sup>-1</sup>), large HACs over the entire section reduced the cross-sectional area of the specimen. This reduced cross-section decreases the engineering stress level that could be obtained. The engineering stress of the hydrogen charged steel was for example higher at low strains but dropped to a similar level as the reference test in air at high strains for as-received 304L tested at 3.3E-2 s<sup>-1</sup>. Wang et al. [329] discussed the influence of extensive HAC formation on the true stress for an austenitic twinning-induced plasticity steel. The authors proposed to use the force divided by the ductile fracture area instead of using the total area, however, this still results in a discrepancy with reality. A suitable way to treat cases with extensive crack formation is not yet well established.

The volume expansion associated with the martensitic transformation was stated to postpone the nucleation of voids or microcracks and to hinder the propagation of cracks [340]. Xiong et al. [341] showed through finite element modelling that in the absence of hydrogen, the volume expansion positively influenced the crack tip propagation since the compressive stresses introduced at the crack tip retard plastic strain. With hydrogen, however, since the volume expansion aggravated the size of the stress field at crack tips, crack propagation will probably increase when the α'-martensitic transformation occurs. The intermediate transformation to ε-martensite, however, was found to result in a more compatible strain evolution preventing the nucleation and growth of hydrogen-assisted cracks [145]. Teus et al. [144] also concluded that the ε-martensite transformation retards localized deformation which increased the cracking resistance. Koyama et al. [146] stated that the ε-martensite/austenite interface could arrest microcrack propagation although it also served as a preferential crack initiation site. The beneficial effect of hydrogen-enhanced martensitic transformations might thus be dual: (i) it increases work hardening which postpones necking and (ii) it hinders crack propagation because of the introduction of ε-martensite.

A competition thus exists between HE and hydrogen-enhanced strain-induced martensitic transformations in 304L ASS resulting in the observed final elongation and strength level at fracture. The negative contributions prevailed in the present work for every tested condition. The dominating HE mechanism (HEDE, HESIV, HELP) might differ for the tested engineering strain rates. Due to the limited time for diffusion, the ability of hydrogen to assist crack propagation is more limited at high strain rates. It should be noted that the HEDE mechanism does not necessarily need large-scale hydrogen diffusion leading to accumulation of hydrogen at crack tips since the hydrogen concentration in the present work was high from the start and might already have exceeded the critical value for decohesion at low stresses. The abundant presence of HACs on the surface of as-received 304L ASS tested at 3.3E-2 s<sup>-1</sup> proved this statement. Most likely, the HEDE mechanism dominates at high strain rates and hydrogen concentrations, while the plasticity-mediated mechanisms (HELP, HESIV) increase in importance at lower strain rates. The size of the enhanced strain-induced martensitic transformation effect depends on the hydrogen concentration whereby a higher hydrogen concentration increases the amount of martensite.

Possibilities remain for optimizing the balance between HE and enhanced martensitic transformations in austenitic stainless steels. A steel in which hydrogen enhances martensitic transformations but shows low HE and crack initiation sensitivity, as such sustaining the plastic stress until the plastic instability condition is satisfied, could lead to improved strength/ductility combinations. As the transformations that occurred in the near surface region in the present work are not expected to influence the macroscopic stress/strain behaviour largely, moderate hydrogen concentrations should be able to favour martensitic transformations through the entire cross-section in order to have a macroscopic effect. As long as the main martensite fraction upon transformation consists of a'-martensite with a high hydrogen diffusivity, achieving drastic improvement in HE resistance will probably be challenging. Due to the microcrack arrestability, the large strain compatibility with the matrix and the low hydrogen diffusivity of  $\varepsilon$ martensite [55], the  $\gamma \rightarrow \epsilon$ -martensite transformation route should be preferred. The hexagonal close packed (HCP) structure has, however, a lower stress accommodation capacity which means that the ductility of the formed ε-martensite phase is key in maximizing the positive effect [342]. The possible outcome could be similar to the observation by several authors that the presence of hydrogen increased the elongation at fracture in FCC materials by promoting deformation twinning [343, 344, 345]. Both electrochemical and gaseous hydrogen charging were applied in these studies. Deformation twinning is an alternative deformation mechanism and can be treated similarly as *ɛ*-martensite with respect to the dislocation processes governing the nucleation and growth. Ogawa et al. [345] state that they were the first to establish prevailing beneficial hydrogen effects in a commercially-available stable austenitic steel. The authors also concluded that the hydrogen concentration was very important for the final elongation at fracture; more hydrogen (up to 133 wppm) leading to a higher twin fraction and consequently a higher elongation in their work.

#### 7.4. Effect of mechanical polishing after hydrogen precharging on the embrittlement

Mechanical polishing (3 µm and 1 µm diamond paste for five minutes in total) was applied to seven days electrochemically hydrogen charged 304L ASS immediately after the charging procedure, i.e. while high hydrogen concentrations were still present in the surface regions. Figure 7-12 illustrates the effect of the mechanical polishing step in the presence of hydrogen on the microstructure. Slip bands (cf. image quality map) and a small fraction of a'-martensite with a clear planar appearance (cf. phase map) were observed on the specimen surface. When no mechanical polishing was applied, slip bands were already observed as presented in Figure 6-4. The high hydrogen concentration in the steel lattice from the electrochemical charging procedure decreased the shear modulus in such a way that the internal stress and the stress exerted by hydrogen were able to evoke dislocation migration. No martensitic transformations were, however, observed. When additional stress was applied by mechanical polishing and when the austenite stability was reduced by the high hydrogen concentration during polishing, a'-martensitic transformations occurred on top of dislocation nucleation and migration.



Figure 7-12: Image quality and phase map of the polished surface immediately after 7 days electrochemical precharging

The influence of the additional polishing step on the surface hardness was measured to validate whether the amount of surface defects increased. Vickers hardness measurements were performed on the hydrogen charged specimen and on the hydrogen charged and polished specimen. To limit the depth of the indent and as such remain in the surface region, a weight of 20 grams was used for the hardness tests. Figure 7-13 shows the results of the hardness measurements for different experimental conditions. The surface hardness increased largely in the presence of hydrogen (225 HV to 382 HV) as a result of the solid solution hardening effect. After mechanical polishing, the hardness increased to 410 HV, i.e. an increase of approximately 30 HV which can be linked to an increased defect concentration. After hydrogen effusion for two weeks, a permanent hardness increase of 40-50 HV was observed, most likely as a result of the

#### Chapter 7

increased dislocation density after charging. When the 304L ASS was polished immediately after hydrogen charging, the permanent hardness increase was 50-60 HV. This difference is more or less similar as when no polishing was applied. The polishing procedure possibly removed some of the slip bands and at the same time introduced new permanent plastic deformation features. Figure 7-14 indicates that the surface defect concentration affects the elongation at fracture that can be reached during in-situ mechanical testing. A strain rate of 1E-3 s<sup>-1</sup> was used for this purpose. Due to the additional polishing step, the transport time to the environmental cell was increased by 7 minutes (12 minutes in total). A higher fraction of defects most likely increased the amount of stress concentrations and enhanced hydrogen-assisted crack initiation and propagation. As a result, earlier fracture occurred. The effect is most likely comparable with the prestrained 304L ASS results where the defect concentration was enlarged over the entire specimen thickness while only the surface layer was affected here. As the additional polishing step aggravated the mechanical response, the research strategy followed throughout the PhD, i.e. without additional polishing, is more appropriate for the HE sensitivity evaluation.



Figure 7-13: Vickers surface hardness measurements (weight = 20 grams) for different experimental conditions



Figure 7-14: Engineering stress-strain curves of 304L ASS with polishing only before (= polished) or before and after hydrogen precharging (= repolished)

## 7.5. <u>Conclusions</u>

The HE sensitivity of as-received and 30% tensile prestrained AISI 304L ASS was evaluated by tensile testing at different constant crosshead displacement rates. The following conclusions can be drawn:

- The lower the crosshead displacement rate, the more the alloy was embrittled as hydrogen was given more time to diffuse and accumulate. As a consequence of the increased time for diffusion, the size of the embrittled zone on the fracture surface increased with decreasing strain rate as well. Hydrogen reached deeper into the specimen than expected from the initial hydrogen diffusivity amongst others due to the continuously increasing a'-martensite fraction.
- Prestraining increased the HE sensitivity at every crosshead displacement rate due to the presence of defects at the surface and possibly also the faster increase of the a'-martensite fraction with strain. Defects at the surface were found to have an effect on the final elongation.
- Hydrogen-assisted cracking appeared early in the experiment from a strain perspective and increased in size depending on the amount of strain that could be reached at fracture.
- At an engineering strain rate of 3.3E-2 s<sup>-1</sup>, an increase in elongation at fracture was observed for as-received 304L ASS tested in-situ with hydrogen compared to the reference air test. Compared to the reference test in solution, hydrogen embrittlement was observed. This observation was a result of the restriction of the adiabatic heating effect in solution. HE of unstable austenitic stainless steels should thus be evaluated at comparable conditions, i.e. both in air or both in solution, for fast strain rates (>1E-3 s<sup>-1</sup>).
- Enhanced martensitic transformations were observed at the surface in the presence of hydrogen. Apart from an increased α'-martensite fraction, ε-martensite was additionally formed. A reduction in stacking fault energy and austenite stability were held responsible. The effect of hydrogen can be regarded as a positive hydrogen contribution to the mechanical response of 304L ASS. The negative hydrogen contributions, however, prevailed. A schematic representation of the balance is shown in Figure 7-15.



Figure 7-15: Schematic representation of the balance between the positive and negative contributions of hydrogen on the mechanical properties of 304L ASS

## Chapter 8 Critical evaluation of the hydrogen interaction with twinning induced plasticity (TWIP) steel: effect of aluminium addition

#### 8.1. Introduction

Twinning-induced plasticity (TWIP) steels have an FCC crystal structure at room temperature and are part of the second generation advanced high strength steels. The most important alloying element is manganese with typical additions in the range of 17 to 25 wt%. Manganese additions higher than 30 wt% are not desirable as a brittle β-Mn phase is formed [346]. Carbon is typically added to increase the yield strength with values ranging from 0.5 to 0.8 wt%. Aluminium and silicon can be added to increase the formability [347].

Although most of the metallurgical developments for high manganese steels happened the past two decades and are still ongoing intensively, the first knowledge dates from a lot earlier. Already in 1888, Robert A. Hadfield [348] reported the peculiar properties created by manganese when added in large quantities to steel, i.e. 11 to 14 wt%. In 1890, Hadfield patented the process for making this new steel type [349]. His pioneering work on Hadfield steel was pursued by Hall [350] and Krivobok [351] in 1929 who described the microstructure in detail which was entirely austenitic at room temperature. In 1936, Tofaute and Linden [352] developed a quideline for the required carbon and manganese level to stabilize austenite at room temperature: wt% Mn + 13 wt% C  $\geq$  17. It took until 1935 for someone to mention the evolution of the microstructure with plastic strain at room temperature. Chévenard [353] assumed the formation of a hard phase during straining. A few years later, Troiano and McGuire [354] concluded that two types of martensite could form by the mechanical induced phase transformation of austenite, i.e. a hexagonal εmartensite phase and a tetragonal g'-martensite phase. The hexagonal e-martensite phase was already discovered by Schmidt [355] in 1929 in binary Fe-Mn alloys with manganese contents of 12 to 29 wt%. In the fifties, the occurrence of mechanical twinning was claimed to explain the high work hardening rate of Hadfield steel that did not contain any ε- martensite [356]. The presence of twins was formally confirmed by TEM studies in the sixties, e.g. [357]. In the seventies, researchers got interested in steels containing more manganese and less carbon than the Hadfield steel, e.g. [31]. This resulted in many patents in the early nineties. European steelmakers such as ThyssenKrupp and Usinor (later ArcelorMittal) got involved in the patenting in the late 90s [36]. The commercialisation of TWIP steels is, however, still in its infancy.

TWIP steels possess a high potential to become important automotive materials due to their unique combination of strength and ductility. Due to high alloying additions, TWIP steels are typically lighter than conventional steels as well. Its high strength makes them ideal for structural reinforcement [29]. The superior ductility results in easy press-forming. TWIP steels perform better than titanium stabilised

### H interaction with TWIP steel

interstitial free steel which is considered as one of the most formable BCC steel types [29]. Finally, TWIP steels exhibit a large energy absorption potential improving crashworthiness. A feasibility study additionally showed that TWIP steels are very cost effective for energy absorption applications [358]. Until now, TWIP steels have only been used in a few applications, such as the front bumper of the 2012 FIAT Panda (see Figure 8-1) [359]. TWIP steels are already patented for use in oil, gas and petrochemical industry [360]. Due to their high erosion corrosion resistance, TWIP steels can be used as pipeline steels for transport of oil sands. TWIP steel have excellent cryogenic properties making them ideal for liquefied natural gas (LNG) transportation as well. Posco (South-Korean steelmaking company) and DSME (South-Korean shipbuilding company) developed, for example, a new high-manganese steel for applications at extremely low temperatures. The material is 53% more cost effective compared to existing cryogenic materials [361].



## Figure 8-1: TWIP steel bumper beam of FIAT Panda, first commercialised automotive product (2012) [359]

The poor resistance to aqueous corrosion of TWIP steels, however, largely favours hydrogen absorption in the presence of moisture [362]. It is, therefore, of crucial importance to study the interaction between hydrogen and the microstructure of TWIP steels, where the hydrogen solubility and diffusivity are two important parameters. The chemical composition of TWIP steels was found to significantly influence both the hydrogen solubility and diffusivity. Ismer et al. [363] performed ab initio DFT calculations to reveal the influence of the manganese content on the hydrogen solubility and mobility. It was found that manganese increased both parameters. The authors also reported that carbon concentrations below 3 at% had no influence on hydrogen diffusion nor on the solubility as regions with compressive and tensile strain cancelled each other.

One of the most promising alloying elements to improve the resistance of TWIP steels to hydrogen-related degradation is aluminium [364]. Contradictory findings are reported in literature regarding the influence of aluminium on the hydrogen solubility of TWIP steels. Aluminium was stated to cause a reduction of the hydrogen absorption by several authors. Park et al. [365] stated, e.g., that a lower hydrogen concentration was caused by the formation of a protective Al-containing surface layer as they observed an α-Al<sub>2</sub>O<sub>3</sub> layer
below the (Fe<sub>0.8</sub>Mn<sub>0.2</sub>)O layer during hydrogen charging of Fe-18Mn-0.6C-1Al and Fe-18Mn-0.6C-2Al TWIP steel. The authors stated that the layer prevented hydrogen from absorbing into the specimens. Guo et al. [366] obtained polarization curves showing that aluminium addition to high manganese steels greatly reduced the corrosion rate in a 5% NaCl solution. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer was held co-responsible for this improved corrosion rate. Koyama et al. [367] also revealed that hydrogen entry was suppressed in the Aladded steel in comparison to an Al-free variant. The authors explained this by a decrease of the trap density in the Al-added steel. Unfortunately, aluminium was also reported to increase hydrogen absorption. Ryu et al. [368] reported an increase in the hydrogen concentration with the addition of aluminium. The steels were, however, not charged to a homogeneous hydrogen concentration through the thickness. The effect of a differing hydrogen diffusivity could thus not be excluded. Based on DFT calculations, Song et al. [369] found that aluminium atoms in TWIP steel caused a localized dilation that better accommodated hydrogen. Their trapping theory indicated both that the presence of aluminium allowed the TWIP steel to absorb more hydrogen compared to an Al-free steel and that the diffusion coefficient was significantly affected by the presence of aluminium as well, i.e. lowered compared to an Al-free TWIP steel. Hüter et al. [370] similarly calculated that the presence of aluminium decreased the hydrogen diffusion coefficient at room temperature by approximately one order of magnitude. Han et al. [73] also reported that 1.5 wt% of aluminium added to an Fe-18Mn-0.6C TWIP steel decreased the permeability and diffusivity of hydrogen and increased its solubility. The authors performed high temperature hydrogen permeation tests using gaseous hydrogen charging to obtain these results. The ultrahigh vacuum used during the test prevented the formation of an oxide layer that could affect hydrogen absorption. The authors, therefore, stated that their results reflected the inherent bulk influence of aluminium on hydrogen diffusivity and solubility.

In this chapter, the hydrogen solubility and diffusivity of TWIP steels with different manganese contents will be investigated to verify the findings reported based on DFT calculations. The effect of the addition of aluminium will be addressed as well since contradictory results were reported. Moreover, literature clearly showed a lack of temperature-dependent hydrogen diffusion coefficients for TWIP steels. This work, therefore, aims to provide these equations through analysis of thermal desorption spectra

#### 8.2. <u>Alloy selection and characterization</u>

Three different TWIP steel compositions were casted. Fe-18Mn-0.6C TWIP steel, hereafter designated as '18Mn', served as reference alloy since this alloy was frequently studied in literature as well. To elucidate the effect of aluminium on the hydrogen solubility and temperature-dependent effective hydrogen diffusion coefficient, 1.5wt% aluminium was added to the reference alloy, i.e. Fe-18Mn-0.6C-1.5Al TWIP steel, later on referred to as '1.5Al'. The influence of an increased manganese fraction was investigated as well. The manganese content was chosen as such to have an equal stacking fault energy as the Al-added TWIP steel. The equal SFE will mainly be of importance in Chapter 9 where the influence of hydrogen on the mechanical properties will be evaluated. Fe-24.5Mn-0.6C TWIP steel was hence casted, further on referred to as '24.5Mn'. A subregular solution thermodynamic model proposed by Saeed-Akbari et al. [21] was used to predict the SFEs of the alloys. The model is able to calculate the SFE of high manganese steels (10-35 wt%) with carbon concentrations of 0 to 1.2 wt% and is the most widely used method to explain the observed properties of high-manganese steels. More details on the model are given in the next part of this section followed by a general microstructural characterisation of the three alloys.

According to Adler et al. [371], the intrinsic SFE [mJ/m<sup>2</sup>] of FCC alloys can be calculated as follows:

$$SFE = 2 \cdot \rho \cdot \Delta G^{\gamma \to \varepsilon} + 2 \cdot \sigma^{\gamma/\varepsilon}$$
(8-1)

In this equation,  $\rho$  is the molar surface density along the {111} planes [mol/m<sup>2</sup>],  $\Delta G^{\gamma \rightarrow \epsilon}$  is the free energy change for the transformation of austenite to  $\epsilon$ -martensite [J/mol] and  $\sigma^{\nu/\epsilon}$  is the  $\nu/\epsilon$  interfacial energy [mJ/m<sup>2</sup>].

The molar surface density p [mol/m<sup>2</sup>] along the {111} planes can be calculated as follows [27]:

$$\rho = \frac{4}{\sqrt{3}} \frac{1}{a^2 N}$$
(8-2)

where a is the lattice parameter [m] of the alloy and N is Avogadro's number [mol<sup>-1</sup>]. The lattice parameter of austenite is calculated based on the composition dependent equation of Babu et al. [372]:

$$a_{0\gamma} = (3.5780 + 0.033X_{C} + 0.00095X_{Mn} + 0.0056X_{Al})^{*1E-10}$$
 (8-3)

where X<sub>i</sub> is the molar fraction of the component i. For the sake of simplicity, the influence of other alloying elements given by Babu et al. [372] was not reported. The temperature dependence of the lattice parameter is given by the equation of Garcia de Andres et al. [373].:

$$a_{\gamma} = a_{0\gamma}(1 + \beta_{\gamma}(T - 300))$$
(8-4)

In this equation,  $\beta_{\gamma}$  is the linear thermal expansion coefficient of austenite equal to 2.065x10<sup>-9</sup> K<sup>-1</sup> and T (K) is the temperature.

The free energy  $\Delta G$  [J/mol] comprises of various terms [21]:

$$\Delta G^{\gamma \to \varepsilon} = X_{Fe} \Delta G_{Fe}^{\gamma \to \varepsilon} + X_{Mn} \Delta G_{Mn}^{\gamma \to \varepsilon} + X_{Al} \Delta G_{Al}^{\gamma \to \varepsilon} + X_C \Delta G_C^{\gamma \to \varepsilon} + X_{Fe} X_{Mn} \Delta \Omega_{FeMn}^{\gamma \to \varepsilon}$$
$$+ X_{Fe} X_{Al} \Delta \Omega_{FeAl}^{\gamma \to \varepsilon} + X_{Fe} X_C \Delta \Omega_{FeC}^{\gamma \to \varepsilon} + X_{Mn} X_C \Delta \Omega_{MnC}^{\gamma \to \varepsilon} + \Delta G_{mag}^{\gamma \to \varepsilon}$$
(8-5)

 $\Delta\Omega_{i,j}^{\gamma \to \varepsilon}$  is the interaction energy between two components i and j [J/mol],  $\Delta G_{mag}^{\gamma \to \varepsilon}$  is the free energy contribution due to the magnetic transition [J/mol]. The values of  $\Delta G_i^{\gamma \to \varepsilon}$  and  $\Delta\Omega_{i,j}^{\gamma \to \varepsilon}$  were found in [21]. The interactions Mn-Al and Al-C are assumed to be negligible in an iron-rich alloy. The contribution of the magnetic transition can be evaluated as follows:

$$\Delta G_{\text{mag}}^{\gamma \to \varepsilon} = G_{\text{mag}}^{\varepsilon} - G_{\text{mag}}^{\gamma}$$
(8-6)

$$G_{\text{mag}}^{i} = R \cdot T \cdot \ln\left(1 + \frac{\beta^{i}}{\mu B}\right) \cdot f(\frac{T}{T_{N}^{i}})$$
(8-7)

where  $\beta^i$  is the magnetic moment of phase i,  $T_N^i$  is the Néel temperature of phase i and  $\mu B$  is the Bohr magneton. The function f (T/  $T_N^i$ ) is given by the following polynomial:

$$f = -\frac{\frac{(T_N)^{-5}}{10} + \frac{(T_N)^{-15}}{315} + \frac{(T_N)^{-25}}{1500}}{D}$$
(8-8)

D = 2.34 for the fcc and hcp phases. All necessary values to calculate the free energy contribution are summarised in Table 8-1.

Table 8-1: Values necessary to calculate the free energy contribution to the SFE [21]

Parameter [unit]	Equation or value from literature
$\Delta \mathrm{G}_{\mathrm{Fe}}^{\gamma  ightarrow \epsilon}$ [J/mol]	-1828.4+4.686T
$\Delta G_{Mn}^{\gamma  ightarrow \epsilon}$ [J/mol]	3970 <b>-</b> 1.7T
$\Delta G_{Al}^{\gamma  ightarrow \epsilon}$ [J/mol]	5481.04-1.799T
$\Delta G_C^{\gamma \to \epsilon} \text{ [J/mol]}$	-24595.12
$\Delta\Omega_{FeMn}^{\gamma ightarrow \epsilon}$ [J/mol]	-9135.5+15282.1 Х <sub>Мл</sub>
$\Delta\Omega_{ m FeAl}^{\gamma ightarrow \epsilon}$ [J/mol]	3323
$\Delta\Omega_{ m FeC}^{\gamma ightarrow\epsilon}$ [J/mol]	42500
$\Delta\Omega_{\mathrm{MnC}}^{\gamma ightarrow \epsilon}$ [J/mol]	26910
$\frac{\beta^{\gamma}}{\mu B}$ [-]	0.7 X <sub>Fe</sub> +0.62 X <sub>Mn</sub> -0.64 X <sub>Fe</sub> X <sub>Mn</sub> - 4 X <sub>C</sub>
$\frac{\beta^{\varepsilon}}{\mu B}$ [-]	0.62 X <sub>Mn</sub> – 4 X <sub>C</sub>
$T_N^{\gamma}$ [K]	250 ln(X <sub>Mn</sub> )-4750 X <sub>C</sub> X <sub>Mn</sub> -6.2 X <sub>Al</sub> +720
$T_N^{\epsilon}$ [K]	580 X <sub>Mn</sub>

# H interaction with TWIP steel

The interfacial energy is stated to belong to the interval  $13 < \sigma^{\forall \epsilon} < 20 \text{ mJ/m}^2$  for Fe-Mn systems. A constant value of 15 mJ/m<sup>2</sup> was chosen in the present calculations. This value is, however, not exact, resulting in a possible error in the calculated values. Table 8-2 shows the resulting SFE for the three TWIP steels. The steels were hot rolled at 1100 °C with heating in between the passes and subsequently water quenched. A final plate thickness of 2 mm was obtained. Several authors experimentally determined the SFE of some of the alloy compositions studied in this work. Kim et al. [374] used, for example, TEM and found a SFE value of  $13 \pm 3 \text{ mJ/m}^2$  for 18Mn while 1.5Al showed a SFE of  $30 \pm 10 \text{ mJ/m}^2$ . Jin et al. [375] determined the SFE through XRD and found a value of  $17\pm3 \text{ mJ/m}^2$  for 18Mn and  $29\pm5 \text{ mJ/m}^2$  for 1.5Al. These experimental values are all in agreement with the ones calculated in this work, cf. Table 8-2. No experimental data was found for the SFE of the 24.5Mn TWIP steel. However, this steel composition was specifically designed in this work to evaluate the role of the SFE in the beneficial effect of aluminium on the HE sensitivity of TWIP steels.

	Fe-18Mn-0.6C	Fe-18Mn-0.6C-1.5Al	Fe-24.5Mn-0.6C
SFE [mJ/m²]	16.24	29.63	29.81

Table 8-2: Thermodynamic SFE calculation for the three prepared alloys<sup>12</sup>

Figure 8-2 shows ND IPF maps of the three TWIP steels. High angle grain boundaries are indicated in black and annealing twin boundaries ( $\Sigma$ 3 boundary characterised by a 60 degree rotation around <111>) are indicated in white. Equiaxed grains were observed for every alloy with random crystallographic orientations, i.e. no clear texture was present. The average grain size (diameter) of the alloys was determined based on the EBSD measurements as 17.4 ± 8.9 µm, 22.6 ± 10.6 µm and 16.9 ± 8.2 µm for the 18Mn, 1.5Al and 24.5Mn TWIP steel, respectively. The 1.5Al TWIP steel had a slightly larger average grain size while the other two alloys showed a comparable grain size, which is also visually detectable in Figure 8-2.

Throughout the entire cross-section of the three alloys, inclusions were observed which were oriented parallel to the rolling direction. An example SE image for the 18Mn TWIP steel is shown in Figure 8-3. An EDX mapping confirmed the abundant presence of manganese and sulphur, i.e. MnS inclusions were formed. Equal size SE images were taken through the thickness of the specimens to quantify the MnS inclusions. On average, 14.6  $\pm$  5.3, 15.3  $\pm$  3.3 and 12.9  $\pm$  5.9 MnS inclusions were counted on an area of 160x180 µm<sup>2</sup> for the 18Mn, 1.5Al and 24.5Mn alloy, respectively, i.e. a comparable fraction of inclusions for all alloys that did not differ significantly through the thickness.

<sup>&</sup>lt;sup>12</sup> Prof. Springer is acknowledged for the provided material (active at Max-Planck-institut für Eisenforschung (GmbH) Düsseldorf and RWTH Aachen University)



Figure 8-2: ND IPF maps of the three TWIP steels, high angle grain boundaries are indicated in black and Σ3 annealing twin boundaries in white



Figure 8-3: MnS were found homogeneously distributed in the bulk of the three TWIP steels, SE image and EDX map as example for 18Mn

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#### 8.3. <u>Alternative electrochemical charging procedures</u>

Difficulties arose when the same charging procedure was applied as for the stainless steel types discussed in the previous chapters. Although a cathodic current was applied, the surface integrity was still largely affected due to the low corrosion resistance of TWIP steels. Consequently, the prolonged charging times resulted in a substantial weight reduction due to surface corrosion. The surface appearance after a charging time of seven days is illustrated in Figure 8-4 (a). The hydrogen concentration in the 18Mn steel was measured with melt extraction after different charging times. The result can be found in Figure 8-4 (b). Every measurement is reported as a separate dot. The hydrogen concentration first increased but eventually decreased with time to similar values as when no hydrogen charging was applied. Most likely, with prolonged time, the corrosion rate could keep up with the hydrogen diffusion speed at room temperature, continuously dissolving the hydrogen charged zone. Therefore, alternative and less invasive solutions were used for the electrochemical charging procedure of TWIP steels in this and the next chapter. The alternative charging procedure will be discussed in the relevant sections.



Figure 8-4: (a) SE image of surface appearance after seven days charging in sulphuric acid at 0.8 mA/cm<sup>2</sup>, (b) hydrogen concentration as a function of charging time in sulphuric acid for 18Mn

#### 8.4. Evaluation of the hydrogen solubility and diffusivity of the three TWIP alloys with TDS

The effective hydrogen diffusivity and equilibrium hydrogen concentration of the three TWIP steels were assessed with thermal desorption spectroscopy in a similar way as was done in chapter 4 and chapter 6. In order to reach a nearly homogeneous hydrogen concentration, the specimen thickness was reduced to 0.2 ± 0.01 mm. The charging temperature was also increased to 80°C to allow faster hydrogen diffusion. In order to do this, the used electrolyte should be stable at 80°C. An electrolyte frequently reported in literature on TWIP steels which better preserves the surface from corroding, is 0.1M NaOH containing 3 g/l ammonium thiocyanate. A current density of 5 mA/cm² is typically used. The charging time was chosen based on preliminary diffusivity simulations using the model described in chapter 4. Due to a lack of temperature-dependent hydrogen diffusion coefficients for TWIP steels in literature, the equation determined in the work of Xiukiu et al. [74] for austenitic stainless steel types was used for the simulation. The different atomic arrangement (Mn instead of Cr and Ni alloying) was therefore unfortunately neglected in the preliminary simulation. Figure 8-5 presents the hydrogen concentration profile through the cross section after charging. As Han et al. [73] suggested a higher diffusivity for TWIP steels at room temperature (order of magnitude of 5E-15 m<sup>2</sup>/s) compared to the value for austenitic stainless steels [74]. it is reasonable to assume that the charging procedure at 80°C might result in an even closer approximation of a homogeneous hydrogen concentration for TWIP steels. Heating rates of 600 K/h and 900 K/h were used for the TDS experiments.



Figure 8-5: Preliminary simulation of the normalised hydrogen concentration profile after charging for seven days at 80°C, model description can be found in chapter 4

The experimental TDS data can be found in Figure 8-6. Two curves are represented for each TWIP steel, i.e. one for the heating rate of 600 K/h and one for the heating rate of 900 K/h. All curves have a similar appearance consisting of one asymmetrical peak in the low temperature regime. In Figure 4-15, it was shown that this peak shape is typically observed in metals characterised by a low hydrogen diffusivity charged to a (nearly) homogeneous hydrogen concentration through the thickness.



Figure 8-6: TDS data after seven days charging at 80°C in 0.1M NaOH with 3 g/l NH<sub>4</sub>SCN at 5 mA/cm<sup>2</sup> for (a) 18Mn, (b) 1.5Al and (c) 24.5Mn, specimen thickness = 0.2 mm

Similar to the approach in chapter 4 and chapter 6, the experimental TDS data will be fitted with a numerical model based on Fick's diffusion laws to extract the temperature-dependent effective hydrogen diffusivity and the equilibrium hydrogen surface concentration. The optimal fitting parameters were determined by using both heating rates in a least squares regression. The fits are included in Figure 8-7 for all tests performed at a heating rate of 600 K/h. The entire curve was used in the fitting procedure since the electrochemical charging procedure used in this work did not result in a large surface concentration due to the clear absence of hydrogen effusion in the first part of the curve (below 100°C). The fitting parameters are presented in Table 8-3.  $C_s$  represents the equilibrium surface concentration,  $D_0$  the pre-exponential factor and Q the activation energy of the temperature-dependent effective hydrogen diffusion coefficient D.



Figure 8-7: Diffusion model fit to the experimental TDS data of Figure 8-6 of homogeneously charged TWIP steels, (a) 600 K/h, (b) 900 K/h, specimen thickness = 0.2 mm

	C <sub>s</sub> [wppm]	D₀ [m²/S]	Q [J/mol]	D at RT (298K) [m²/s]
18Mn	50.66	5.15E-6	57473	4.34E-16
1.5Al	55.76	5.95E-6	58446	3.38E-16
24.5Mn	55.52	5.97E-6	57433	5.11E-16

Table 8-3: Diffusion fit parameters for the experimentally obtained TDS data

The equilibrium hydrogen concentration  $C_s$  as determined from the fit of the TDS data was clearly different for the three TWIP steel compositions. Firstly, in the present work, the three TWIPS steels have a carbon content of approximately 2.7 at%. Hydrogen diffusion and solubility should thus not be affected by the carbon concentration in solid solution since Ismer et al. [363] reported that no effect can be expected with carbon concentrations below 3 at%. Both the addition of manganese and the addition of aluminium increased the hydrogen solubility. It was suggested in literature that aluminium interfered in the oxide layer and therefore reduced hydrogen absorption. Many other authors reported, however, that the solubility increased with the addition of aluminium as determined through both experiments and DFT calculations. The reason for the increase in solubility is most likely the increased lattice parameter in the neighbourhood of aluminium atoms [369]. An increase in the hydrogen solubility could hence be confirmed as the intrinsic effect of the addition of aluminium in TWIP steels. The addition of 1.5 wt% aluminium increased the hydrogen concentration by 10% in the present work. Han et al. [73] reported an increase of 11% with high temperature hydrogen permeation experiments for 1.5AL TWIP steel which is consistent with the value found in the present work. The observation of an increased hydrogen solubility with increasing manganese content is consistent with the DFT calculations in literature as well indicating more lattice space due to the slightly larger atomic radius of manganese compared to iron [363]. The effect of manganese addition led to a similar increase in hydrogen concentration compared to the effect of aluminium addition in the present work. A higher fraction of manganese was, however, added making it invalid to directly compare the effects of both elements on the hydrogen solubility.

Based on the numerical analysis of the TDS tests, the hydrogen diffusivities of the three TWIP steels could be evaluated as well, cf. Table 8-3. Similarly as for the hydrogen solubility, the diffusivity was significantly altered as a function of the chemical composition of the TWIP steels. Aluminium addition clearly decreased the hydrogen diffusivity at room temperature, while the addition of manganese increased the hydrogen diffusivity compared to the 18Mn reference TWIP steel (cf. D at RT in Table 8-3). Han et al. [73] reported a hydrogen diffusion coefficient of 7.11E-15 m<sup>2</sup>/s for 18Mn and 4.62E-15 m<sup>2</sup>/s for 1.5Al at room temperature through extrapolation of high temperature gaseous hydrogen permeation data, i.e. a 35% decrease in diffusivity with the addition of 1.5 wt% aluminium. The values found in the present work are slightly lower but a comparable decrease (22%) was obtained for the values at room temperature. Ismer et al. [363] mentioned that for manganese concentrations higher than 20 wt%, long-range percolating Mn chains are present characterised by efficient hydrogen diffusion due to volumetric effects. This effect most likely explains the increase in hydrogen diffusivity with the addition of manganese. The normalised hydrogen concentration profile was evaluated through the thickness after the charging procedure for the three TWIP steels with the data reported in Table 8-3. Figure 8-8 shows the result of this simulation. The difference in hydrogen diffusivity is reflected in the concentration profiles. All TWIP steels were nearly homogeneously charged with a hydrogen concentration of more than 80% of the surface equilibrium concentration in the center, which is clearly higher than the simulated value for stainless steel in Figure 8-5.



Figure 8-8: Normalised hydrogen concentration profile for the three TWIP steels after charging for seven days at 80°C based on numerical simulation of TDS data

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# 8.5. <u>Conclusions</u>

Three different TWIP steels were studied with as main goal to investigate the influence of the chemical composition on the hydrogen solubility and diffusivity. The reference alloy was Fe-18Mn-0.6C TWIP steel. Two alternative TWIP steels were investigated: one with an increased aluminium content (Fe-18Mn-0.6C-1.5Al TWIP steel) and one with an increased manganese content (Fe-24.5Mn-0.6C TWIP steel). The hydrogen solubility and effective hydrogen diffusivity of the TWIP steels were evaluated with thermal desorption spectroscopy. The following conclusions were drawn:

- The hydrogen solubility increased with both alloying additions to a similar value. Both additions created more lattice space as such better accommodating hydrogen.
- The hydrogen diffusivity was decreased with aluminium addition and increased with manganese addition. Aluminium thus had a trapping effect slowing down the migration of hydrogen atoms through the lattice.

# Chapter 9 The role of stacking fault energy in the beneficial effect of aluminium on the hydrogeninduced mechanical degradation of twinninginduced plasticity (TWIP) steel

#### 9.1. Introduction

Delayed cracking, i.e. the appearance of cracks after some time associated with the presence of hydrogen and internal stresses, is frequently observed in high-Mn TWIP steels and restricting their applicability [36]. Due to the close relation between delayed cracking and hydrogen embrittlement, large research efforts are devoted to decreasing the HE susceptibility of TWIP steels. Koyama et al. [53] published an overview of the characteristics of HE in TWIP steels. Fracture in the presence of hydrogen was mainly intergranular but often also showed characteristics of quasi-cleavage fracture. The chemical composition of the alloys was stated to be of particular importance since this influences the stacking fault energy (SFE), austenite stability, hydrogen absorption behaviour and hydrogen diffusivity, all of which influence the HE sensitivity. Although many different strategies were already proposed to improve the HE resistance of TWIP steels. the most promising strategy that significantly alleviates the HE sensitivity is the addition of a few percent of aluminium [364]. Mittal et al. [376] stated already in 1994 that Fe-17Mn-0.45C-2.8Al TWIP steel showed only a mild susceptibility to hydrogen-induced degradation. Chun et al. [377] illustrated clearly the effect of aluminium in their work on the influence of various Al contents (0-3.5 wt%) on hydrogen precharged Fe-18Mn-0.6C TWIP steels. They studied the notch fracture stress as a function of the diffusible hydrogen concentration. With increasing diffusible hydrogen concentration, the notch fracture stress of the Al-free steel decreased at a much faster rate than the notch fracture stress of the Al-added steels. The beneficial effect of aluminium was also illustrated by the hydrogen-delayed fracture susceptibility of deep drawn TWIP steel cups. An Al-free TWIP steel showed cracks at the cup edges after exposure to air for seven days while an Al-added variant showed no delayed cracking [378]. The underlying mechanism of the aluminium effect remains, however, to be resolved [364]. Several mechanisms have been proposed in literature which consider either a bulk effect or a surface effect of the addition of aluminium. The main mechanisms found in literature are listed in the following paragraphs.

In a first mechanism, aluminium was stated to increase the SFE and thus reduce the possibility of deformation twin, ɛ-martensite and/or ɑ'-martensite formation which could serve as crack initiation sites. Hong et al. [379] observed a decrease in the amount of twins with increasing aluminium content attributed to the calculated increase in SFE. Chin et al. [378] investigated the effects of aluminium on the deformation and fracture mechanisms of TWIP steel as well. Twinning was more homogeneous and less intense in the Al-added TWIP steel. This was confirmed in tensile tests as the Al-added steel showed a lower work

hardening rate. Koyama et al. [380] supported the theory of aluminium suppressing deformation twinning. Their results clearly revealed the contribution of deformation twins to hydrogen-assisted intergranular and twin boundary cracking. If mechanical twinning was reduced by aluminium addition, the sensitivity of the TWIP steel to intergranular cracking was reduced. Dieudonné et al. [381] equally stated that the increase of the SFE resulted in an enhancement of dislocation cross-slip and a decrease of planar slip. Consequently, a lower stress concentration level was present at dislocation pile-ups at grain boundaries resulting in a lower sensitivity to intergranular cracking. Guo et al. [366] reported that aluminium homogenized deformation twins and suppressed secondary twinning due to the increased SFE. This contributed to the alleviation of hydrogen-delayed fracture of Fe-17Mn-0.6C TWIP steel. Chun et al. [377] observed a higher maximum intensity of the <111> || load direction texture in Al-added TWIP steels which might have decreased the driving force for hydrogen diffusion due to the lower residual stress level and dislocation density. Moveover, the observed texture increased the probability for low-angle grain boundaries that could arrest hydrogen-assisted cracks. The texture was attributed to the high SFE resulting in easy cross-slip and grain rotation. Finally, Kim et al. [269] concluded that aluminium addition suppressed martensitic transformations in TWIP steels because of the increase in SFE as such effectively preventing delayed fracture.

Secondly, aluminium was stated to suppress dynamic strain aging making the material less strong and thus less HE sensitive [382]. Dynamic strain aging is a strengthening mechanism associated with the interaction between dislocations and solute atoms, e.g. carbon, which is commonly observed in TWIP steels during room temperature deformation. Too much work hardening, however, increased the level of residual stress after cold forming and therefore also increased the amount of stress concentration sites. The stress concentration sites attract hydrogen making the microstructure more vulnerable to hydrogen-related damage.

In an alternative mechanism, aluminium was reported to simply reduce the effect that hydrogen exhibits on steels [383]. Hydrogen was stated to reduce the shear modulus thereby leading to a lower critical load for dislocation nucleation. The decrease in shear modulus allowed initiation of dislocation glide at a lower resolved shear stress which is consistent with the HELP mechanism. Aluminium negates some of the capacity of hydrogen to reduce the shear modulus. Alternatively phrased, aluminium reduced the enhancement of the dislocation mobility by hydrogen. The idea was developed using the in-situ nanoindentation technique where the pop-in load was reduced less due to hydrogen in the aluminiumadded TWIP steel.

Finally, the reduced hydrogen absorption in the presence of aluminium has been used to explain the lower HE sensitivity of Al-added TWIP steels as well [365, 366, 367]. Aluminium was, in contradiction, also reported to increase the hydrogen solubility which would increase the HE sensitivity. Therefore, the reduction of the hydrogen diffusivity with the addition of aluminium was put forward to explain the increased HE resistance [73, 369, 370]. A deceleration of the migration of hydrogen results in more time

needed for the accumulation of hydrogen and the generation of hydrogen-assisted cracks. A more elaborate discussion on the effect of aluminium on the hydrogen solubility and diffusivity of TWIP steels was given in section 8.1.

It should be noted that aluminium addition to TWIP steels did not always reduce its sensitivity to hydrogen. The low-cycle fatigue life of hydrogen-charged Fe-17Mn-0.8C-2Al TWIP steel at low strain amplitudes was for example decreased compared to the Al-free variant. Inclusions identified as Al<sub>2</sub>O<sub>3</sub> acted as stress concentration sites ideal for the nucleation of fatigue cracks. At high strain amplitudes, aluminium had a beneficial effect as the higher SFE of the Al-added TWIP steel resulted in more uniform deformation and thus less stress concentrations and local accumulation of hydrogen [384].

In this work, a specific research strategy was designed with major focus on the effect of aluminium on the SFE of TWIP steels, i.e. the first mechanism that was discussed in this introduction. By excluding this parameter from the HE study, it will become clear whether the SFE reduction is the major factor in the enhancement of the HE resistance or whether other mechanisms are more important. The strategy comprised of creating a TWIP steel with a similar SFE as the Al-added variant by increasing the manganese content. The alloy selection based on a thermodynamic model for the SFE can be found in section 8.2. A better understanding of the underlying mechanisms for the enhancement of the HE resistance of TWIP steels will expand the range of applications in which TWIP steels can be used.

#### 9.2. Experimental evaluation of the HE sensitivity of the three TWIP steels

In cup drawing experiments, tensile stresses were found to be most critical for the appearance of delayed cracking in TWIP steels [54]. In the present work, constant extension rate tensile testing was, therefore, performed to evaluate the hydrogen embrittlement susceptibility of the three TWIP steels. The specimens were precharged for seven days and were subsequently tested ex-situ, i.e. in air at room temperature. Reference tests without hydrogen precharging were also performed in air. The sample geometry is given in Figure 3-7. A constant engineering strain rate of 5E-5 s<sup>-1</sup> was used, which is equal or close to strain rates used in literature [181, 269, 385]. The strain was calculated based on the crosshead displacement.

Hajilou et al. [386] proposed an electrolyte that preserves the surface integrity at the nanoscale: a mixture of 1.31 mol/l sodium tetraborate decahydrate (borax,  $Na_2B_4O_7.10H_2O$ ) in glycerol ( $C_3H_8O_3$ ). An adequate conductivity was reached by adding 20 vol% of distilled water. In the present work, this solution was used at a temperature of 50°C and a constant current density of 5 mA/cm<sup>2</sup> was used. The specimens were polished prior to hydrogen charging. It was checked that no damage was introduced at the specimen surface under the applied charging conditions. An advantage of the use of glycerol instead of distilled water, as done in the previous chapter in section 8.4, is the lower oxygen diffusion which decreases the possibility of oxidation even further. Since glycerol decomposes at 80°C, a temperature of 50°C was chosen. With a thickness of 0.7 ± 0.01 mm and a charging time of seven days, no homogeneous hydrogen concentration was obtained through the thickness.

The total hydrogen concentration inside the three TWIP steels before and after hydrogen charging can be found in Figure 9-1. The initial hydrogen concentration from production was similar for the three steels, i.e. approximately 2 wppm. Despite using the same charging conditions, the hydrogen concentration differed significantly between the three TWIP steels after the seven days charging procedure at 50°C. The order is similar as obtained after the nearly homogeneous charging procedure in section 8.4 so the same reasoning applies here. As the values presented here are influenced by the difference in hydrogen diffusivity due to the heterogeneous charging procedure, the difference in hydrogen concentration is slightly more outspoken between the 1.5Al and 24.5Mn TWIP steel since hydrogen diffusion was faster in the latter steel.



# Figure 9-1: Melt extraction results: initial hydrogen concentration, hydrogen concentration after 7 days charging at 50°C in borax/glycerol at 5 mA/cm<sup>2</sup> and their difference (d = 0.7 mm)

The results of the constant extension rate tensile tests can be found in Figure 9-2. Two tests were performed for every condition. A representative tensile curve is shown for every condition. Several enlarged plots are shown in Figure 9-2 as well allowing to identify the influence of the alloy composition and hydrogen presence on the onset of yielding and dynamic strain ageing.

The yield strength (YS) differed slightly between the alloys with the following order based on visual inspection of Figure 9-2: 24.5Mn < 18Mn < 1.5Al. Due to the lack of local strain measurement, the exact yield strength could not be determined. The yield strength of TWIP steels was stated to increase largely with increasing carbon content and to decrease slightly with increasing manganese content in [387]. The following empirical formula was proposed for the yield strength of Fe-Mn-C steels [387]:

YS = 228 +187\*C(wt%) – 2\*Mn(wt%) [MPa] (9-1)

Application of this formula on the 18Mn TWIP steels yields 304 MPa. In the present work, a yield strength of approximately 300 MPa could be observed which is in strong agreement with the proposed formula. Moreover, the formula predicts a drop in the yield strength of 13 MPa for the 24.5Mn TWIP steel compared to the 18Mn TWIP steel. Although the exact difference could not be evaluated, the drop in yield strength with manganese addition was indeed present. As carbon clearly has a large influence on the yield strength, carbon segregation and carbide precipitation lowering the carbon concentration in solid solution might have additionally lowered the yield strength of the 24.5Mn steel compared to the 18Mn steel [388]. Indeed, Liu et al [389] showed that manganese addition accelerated carbon microsegregation in Fe-Mn-C(-Al) TWIP steels. According to [390], aluminium addition leads to solid solution hardening due to lattice distortions and modulus misfit and therefore increased the yield stress by 20 MPa per wt% Al at 293 K. A similar increase in yield strength with aluminium addition was observed in the present work.

Furthermore, dynamic strain aging (DSA) was observed for all materials as serrations on the stress-strain curves starting from the onset of plastic yielding. Detailed images of the observed serrations are presented in the bottom right image of Figure 9-2. Both A type (large periodic serrations) and B type (small quick oscillations) serrations were present for the 18Mn and 24.5Mn TWIP steels, as indicated on the figure. Upon comparison with the types of serrated plastic flow described in [391], the 1.5Al TWIP steel showed a combination of B type and D type (plateaus in the stress-strain curve) serrations leading to less pronounced work hardening compared to A type serrations. In general, DSA is associated with long range diffusion of solute atoms (such as carbon) to temporarily arrested dislocation segments. The segments are subsequently pinned by these solute atoms causing an increase in work hardening. In C-containing TWIP steels, however, DSA typically occurs at room temperature where the carbon diffusion speed is very low and long range diffusion is not possible. DSA in TWIP steels was therefore attributed to the short range reorientation of C-Mn complexes and their interaction with stacking faults enclosed by partial dislocations. Reorientation proceeds via a single diffusion hop of the carbon atom from a tetrahedral interstitial position to the preferred octahedral position after a leading partial dislocation has passed. When the reorientation happens before the trailing dislocation appears, the shear stress for the gliding of the trailing partial dislocation is increased resulting in DSA [392, 393]. Recently, A type serrations were, however, again attributed to long range diffusion of carbon as dislocation pipe diffusion was confirmed with atom probe tomography [393]. The manganese content did not change the DSA phenomenon significantly. The carbon content is most likely the determining factor, which was equal for both alloys. Aluminium clearly reduced the DSA because of the change in serration type and lower amplitude of the serrations. Aluminium is stated to decrease the activity of carbon in high manganese steels. As a result, carbon diffusivity is lowered resulting in less efficient dislocation pinning which is key in order to have dynamic strain aging [394, 395].

Dynamic strain aging was decreased slightly in the presence of hydrogen as can be seen visually in the bottom left image of Figure 9-2. In alpha titanium, it was stated that hydrogen reduced the magnitude of dynamic strain ageing [396]. Hydrogen displaced the phenomenon to higher temperatures and/or lower strain rates. The effect was explained by hydrogen atoms in solid solution preventing other solute atoms from segregating to dislocations. Hydrogen was also stated to decrease the interaction strength of other solute atoms with various defects [396]. The effect is expected to be highest for the 24.5Mn TWIP steel due to the high hydrogen concentration (cf. Figure 9-1) and the intrinsic presence of DSA at room temperature deformation without hydrogen. It is, however, unclear to which extent the DSA reduction influenced the UTS and engineering strain at fracture since many other phenomena played a role as will be discussed later on.



Figure 9-2: Engineering stress-strain curves with and without hydrogen at 5E-5 s<sup>-1</sup>. Top left image summarises all measurements. Magnifications are added to evaluate the onset of yielding (top right image) and DSA (bottom images)

Fast fracture is typically observed in air once necking has initiated in TWIP steels [29] which was also observed in the present work in Figure 9-2. The fracture surfaces of the three TWIP steels with and without hydrogen were investigated with SEM. Figure 9-3 shows representative SE images of the fracture surfaces of the air tests for the three TWIP steels. The fracture surfaces had a very ductile appearance exhibiting many dimples resulting from microvoid coalescence. The non-metallic MnS inclusions gave rise to the larger voids that were frequently observed on the fracture surfaces. The features were clearly oriented parallel to the rolling direction of the steel plates similarly as the MnS inclusions. Moreover, the size of the voids corresponds to the size of the MnS inclusions.

Figure 9-4 shows SE images of the fracture surface near the edges of the specimens that were precharged with hydrogen. The fracture surface of the hydrogen charged specimens presented a distinct appearance compared to the reference specimens. The edge of the specimens showed brittle fracture features while the centre of the specimens were characterised by ductile dimples. The ductile dimples had a similar appearance as the reference air tests presented in Figure 9-3. The central ductile appearance can be explained by a local low hydrogen concentration due to the limited hydrogen diffusion at 50°C after 7 days electrochemical charging. Two types of brittle fracture were observed in the hydrogen-affected zone:

intergranular fracture and guasi-cleavage fracture. The three alloys showed a different amount of each of the two brittle fracture types. In Figure 9-5, more quantitative analyses are presented. Figure 9-5 (a) shows the fraction of intergranular (IG) versus guasi-cleavage (QC) fracture in the H affected zone for the three TWIP steels as determined based on their area in at least two images similar to the ones shown in Figure 9-4. The 1.5Al steel showed mainly quasi-cleavage fracture while the 18Mn and 24.5Mn TWIP steel were more prone to intergranular fracture, the 24.5Mn steel showing the highest fraction of intergranular fracture. Koyama et al. [367] also reported that the fracture mode of an Al-added TWIP steel was guasicleavage while an Al-free steel suffered from intergranular cracking due to hydrogen. The authors stated that as Al suppressed deformation twinning, the local stress concentrations at grain boundaries were reduced, consequently also decreasing the tendency for intergranular fracture. Quasi-cleavage then appears as a result of the suppression of intergranular fracture. Dieudonné et al. [381] also observed that the 18Mn reference TWIP steel was characterised by intergranular fracture in the presence of hydrogen while a mixed inter- and transgranular fracture was observed in 17Mn-0.6C-1.5Al TWIP steel. Song et al. [384] detected a similar change in fracture surface appearance after hydrogen charging. Fe-17Mn-0.8C TWIP steel demonstrated intergranular fracture while the Al-added variant (2 wt%) showed guasi-cleavage fracture. The authors similarly attributed the phenomenon to lower stress concentrations at grain boundaries because of the suppression of deformation twinning.

Koyama et al. [53] mentioned that manganese decreases the cohesive strength of grain boundaries and, therefore, more Mn than needed to get a stable austenitic microstructure in TWIP steels should be avoided as this will assist intergranular cracking in the presence of hydrogen. As a result, although deformation was more homogeneous in the 24.5Mn steel compared to the 18Mn TWIP steel, intergranular fracture was still promoted in the presence of hydrogen. Yang et al. [397] used first principles calculations to determine the influence of manganese on the grain boundary cohesion of the  $\Sigma 11$  grain boundary in austenite. Manganese was found to have an embrittling effect after considering both the chemical effect and the structural relaxation effect. Aluminium, on its turn, reduces the possibility for grain boundary precipitation of (Fe,Mn)<sub>3</sub>C which could be a reason for the marked reduction in intergranular cracking as well [398]. It should be noted that an increased hydrogen concentration was a prerequisite for the appearance of intergranular fracture since this was not observed in the reference air tests. The cohesive strength of grain boundaries was indeed stated to be reduced by hydrogen [399]. In a precipitation hardened Fe-26Mn-11Al-1.2C austenitic steel, for example, hydrogen had an immediate effect in reducing grain boundary cohesion [400]. Since the hydrogen solubility and diffusivity were highest for the 24.5Mn TWIP steel, the hydrogen concentration at grain boundaries was most likely higher as well resulting in a more pronounced grain boundary cohesive strength reduction and thus a higher fraction of intergranular fracture. The hydrogen concentration was, however, not the determining factor since the 18Mn steel exhibited the lowest hydrogen concentration but still revealed a high level of intergranular fracture. This is probably due to the combination of more grain boundary intersections with stacking faults, dislocation pile-ups, twins and  $\epsilon$ martensite plates and a lower grain boundary cohesive strength compared to when aluminium was added.

#### Chapter 9



Figure 9-3: Fracture surface of tensile tests performed in air for the three TWIP steels at 5E-5 s<sup>-1</sup>, images taken at the centre of the fracture surface



Figure 9-4: Fracture surface near the edges of hydrogen charged ex-situ tensile tested TWIP steels at 5E-5 s<sup>-1</sup>, the yellow lines indicate the transition from brittle to ductile fracture features

The average ultimate tensile strength (UTS) and engineering strain at fracture as evaluated from the crosshead displacement with their standard deviation based on all mechanical tests are given in Table 9-1. The loss in strain at fracture and UTS were calculated from these values and are shown in Figure 9-5 (b). Figure 9-5 (c) shows the average thickness of the brittle zone as determined from the distance between the surface and the yellow lines shown in Figure 9-4. To characterise the operational deformation mechanisms, constant extension rate tensile tests were stopped at an intermediate strain value of 30%. Subsequently, the ND plane was analysed with EBSD. For the reference tests in air, phase maps can be found in Figure 9-6. All three alloys showed a fully austenitic microstructure after straining to an engineering strain of 30% in air. Twinning was observed in all three alloys as indicated by the white boundaries in Figure 9-6 ( $\Sigma$ 3 boundary characterised by a 60 degree rotation around <111>). Secondary twinning was observed in the 18Mn TWIP steel as indicated by the white circle in Figure 9-6 where parallel twins were found in more than one direction. Figure 9-7 shows representative phase maps of the

intermediately interrupted tensile tested specimens that underwent hydrogen precharging. The black zones are hydrogen-assisted cracks that appeared on the ND surface. The total twin fraction on the area of the presented images, averaged over two equally sized locations, was determined with the EBSD post-processing software. In order to do this, a partition was first created which excluded points with low confidence index (CI<0.1). Moreover, the lowest image quality points were excluded to account for all points located inside cracks that were not excluded based on the CI threshold. The resulting twin fractions can be found in Table 9-2 and Table 9-3 for the specimens strained without and with hydrogen, respectively. In the presence of hydrogen, martensitic transformations were observed in the 18Mn and 24.5Mn TWIP steels. The martensite fraction (area) was calculated based on the EBSD measurements and added to Table 9-2 and Table 9-3 as well. For the 18Mn TWIP steel, a small fraction of α'-martensite was observed inside larger ε-martensite islands, as indicated by the blue circles. For the 24.5Mn TWIP steel, a small fraction of ε-martensite was observed near a grain boundary as indicated by the yellow circle in Figure 9-7.

	-			
	UTS [MPa]		Engineering strain at fracture [%]	
	Air	Н	Air	Н
18Mn	1058 ± 14	850 ± 28	106.1 ± 1.6	61.9 ± 3.7
1.5Al	894 ± 9	769 ± 23	93.5 ± 4.7	58.2 ± 1.6
24.5Mn	935 ± 5	698 ± 21	97.5 ± 2.5	51.3 ± 2.3

Table 9-1: Average UTS and strain at fracture for the three TWIP steels with and without hydrogen presence
during the ex-situ tensile test at 5E-5 s <sup>-1</sup>



Figure 9-5: Detailed analysis of the engineering stress-strain curves and fracture appearance (a) relative loss in strain at fracture and UTS, (b) thickness of the brittle zone and (c) fracture type distribution (QC= quasi-cleavage and IG = intergranular)



Figure 9-6: Phase map as determined with EBSD on ND plane of uncharged specimens tensile strained to an engineering strain of 30% at 5E-5 s<sup>-1</sup>, twin formation took place (white lines) while no martensitic transformation were observed, the white ellips indicates secondary twinning



Figure 9-7: Phase map as determined with EBSD on ND plane of charged specimens tensile strained to an engineering strain of 30% at 5E-5 s<sup>-1</sup>, both twinning and martensitic transformation are observed, hydrogen-assisted cracks are indicated in black

Table 9-2: Twin boundary and martensite fractions from EBSD measurements on the ND plane of tensile tested specimens until an engineering strain of 30% without hydrogen at 5E-5 s<sup>-1</sup>

Air	Fe-18Mn-0.6C	Fe-18Mn-0.6C-1.5Al	Fe-24.7Mn-0.6C
Twin boundary fraction (%)	16.7	3.9	7.5
٤ martensite fraction (%)	/	/	/
a' martensite fraction (%)	1	1	/

Hydrogen	Fe-18Mn-0.6C	Fe-18Mn-0.6C-1.5Al	Fe-24.7Mn-0.6C
Twin boundary fraction (%)	8.1	13.2	14.6
ε martensite fraction (%)	15	/	0.2
a' martensite fraction (%)	0.3		/

Table 9-3: Twin boundary and martensite fractions from EBSD measurements on the ND plane of tensile tested specimens until an engineering strain of 30% with hydrogen at 5E-5 s<sup>-1</sup>

The values in Table 9-1 indicate a reduction in the UTS with the addition of aluminium. According to [390], the UTS of Fe-18Mn-0.6C-xAl TWIP steel decreased by 100 MPa per wt% Al at 293 K. In the present work, the UTS dropped approximately 160 MPa with the addition of 1.5wt% Al, which is in strong agreement with the proposed drop per wt% Al. Chun et al. [377] also confirmed that Al addition (0-3.5 wt%) resulted in a decrease of the tensile strength in Fe-18Mn-0.6C TWIP steel. The reason for the decrease was proposed to be the reduced work hardening as a result of the increased SFE which disfavours deformation twinning. It was confirmed in Figure 9-6 gualitatively and Table 9-2 guantitatively that the 1.5Al TWIP steel showed a lower twin fraction after deformation in air until an intermediate engineering strain of 30% when compared to the 18Mn TWIP steel. Moreover, DSA was decreased in the presence of aluminium because of the restricted carbon activity which additionally leads to less work hardening. As a consequence of the reduced TWIP effect with aluminium addition, the engineering strain at fracture was also reduced (12.6% strain drop) which is in agreement with the observations in [377]. The UTS and engineering strain at fracture were reduced when the manganese content was increased as well. The UTS value dropped 120 MPa and the engineering strain at fracture dropped 8.6% when comparing 24.5Mn TWIP steel with 18Mn TWIP steel. A similar reasoning as for the addition of aluminium could be used with respect to the extent of deformation twinning observed in Figure 9-6 and reported in Table 9-2. Less deformation twinning was observed due to the increased SFE resulting in a lower work hardening rate. Based on the serrations observed in Figure 9-2, the DSA effect was not altered significantly with the addition of manganese. Unlike with the addition of aluminium, DSA could thus not explain the drop in UTS and engineering strain at fracture when the manganese content was increased.

Although the 1.5Al and 24.5Mn TWIP steel were designed to have equal SFEs, the deformation twin fraction, work hardening and engineering strain at fracture were slightly higher for the 24.5Mn TWIP steel. When considering the grain size effect on the SFE, the 24.5Mn TWIP steel would have a slightly higher SFE due to its lower grain size (16.9 µm for 24.5Mn versus 22.6 µm for 1.5Al leading to a SFE of 33.9 mJ/m<sup>2</sup> and 32.6 mJ/m<sup>2</sup>, respectively) [21]. Contradictory results were, however, observed since the twin fraction was higher for the 24.5Mn TWIP steel. As carbon segregation is enhanced with manganese addition [389] while aluminium reduces the carbon activity [394, 395], the carbon content in solid solution is most likely slightly lower for the 24.5Mn TWIP steel due to carbide precipitation [389, 394, 395]. The carbon content has a strong influence on the SFE of the austenite matrix [388]. A reduction of the carbon content in solid solution is most likely solution leads to a reduction of the SFE according to [21]. Most likely, the slightly lower carbon content in

the austenite matrix of the 24.5Mn steel resulted in a lower SFE compared to the 1.5Al TWIP steel explaining the higher deformation twin fraction and TWIP effect. Moreover, the DSA effect also contributed to the increased work hardening of the 24.5Mn steel since DSA was clearly much less pronounced for the 1.5Al TWIP steel as discussed in the previous paragraphs.

Both the UTS and elongation at fracture were significantly reduced for all alloys in the presence of hydrogen as illustrated guantitatively in Table 9-1 and as a relative loss in Figure 9-5 (b). The relative loss of both mechanical properties was different for the three alloys. The 1.5AL TWIP steel clearly showed reduced HE sensitivity compared to the 18Mn TWIP steel while the 24.5Mn TWIP was prone to a higher HE. The effect of aluminium is thus consistent with most literature observations [364, 376]. Possible, the slightly higher grain size of the aluminium added TWIP steel resulted in a somewhat higher EI than when the grain sizes were equal. Zan et al. [176] investigated the role of grain size on hydrogen embrittlement of Fe-22Mn-0.6C TWIP steel and found that coarser grains resulted in a higher HE susceptibility compared to smaller grains. The authors gave a twofold explanation. First, twin formation starts earlier and a higher density of twins exists in coarser grains. Secondly, per unit of boundary area, a higher diffusive hydrogen concentration is reached with coarser grains. Park et al. [401] similarly stated that grain refinement improved the resistance to HE of Fe-18Mn-0.6C TWIP steel because of a suppression of mechanical twinning. Bai et al. [402] also suggested that grain refinement suppressed HE of Fe-31Mn-3Al-3Si TWIP steel due to the lower hydrogen concentration at grain boundaries in finer grain size specimens. When comparing the active deformation mechanisms with and without hydrogen via the twin and martensite fractions in Table 9-2 and Table 9-3, it is clear that hydrogen decreased the SFE of the three TWIP steels [152, 153, 267]. Hydrogen increased either the twin fraction of the steels (24.5Mn and 1.5Al) or resulted in a shift of the deformation mechanism towards  $\epsilon$ -martensite formation (18Mn) which is preferred at lower SFEs. A hydrogen-enhanced densified twinning (HEDT) mechanism was proposed by Zhang et al. [156] confirming the effect of hydrogen in increasing the twin density and decreasing the twin thickness in TWIP steels. The tendency for twin formation was higher for the 24.5Mn TWIP steel compared to the 1.5Al TWIP steel in the hydrogen charged condition although the SFE was designed to be equal. This could be explained by the higher tendency for twinning without hydrogen as well as by the higher hydrogen concentration present in the 24.5Mn TWIP steel (cf. Figure 9-1). The small fraction of ɛ-martensite observed near a grain boundary in the 24.5Mn TWIP steel was probably the result of the locally reduced SFE by the action of a reduced carbon concentration. Most likely, carbide precipitation occurred at the grain boundaries. Although there seems to be consensus in literature on the effect of manganese in enhancing carbon segregation [389], the grain boundary carbide precipitation should, however, be confirmed by TEM measurements for the alloys studied in the present work.

The depth of the brittle zone on the fracture surface was in the same range for 18Mn and 24.5Mn TWIP steel while 1.5Al showed a distinctly smaller brittle zone (cf. Figure 9-5(c)). The average value was highest for the 24.5Mn steel. The theoretical diffusion depth during both the precharging procedure and the tensile

test time is presented in Figure 9-8 based on the numerical diffusion fit of TDS data in section 8.4 (cf. Table 8-3). Since a different electrolyte was used, another equilibrium surface concentration can be expected. Through numerical simulation of hydrogen charging at 50°C, the fraction of hydrogen that was charged to the steels relative to a homogeneous hydrogen concentration was calculated. The average hydrogen concentrations from Figure 9-1 were subsequently used for the determination of the surface equilibrium concentration. A similar trend in hydrogen solubility can be observed as presented in Table 8-3. however. the percentage difference between 18Mn and 1.5Al was slightly higher in the present case. This is most likely due to experimental variation. The trend in the size of the brittle zone (24.5Mn > 18Mn > 1.5Al) was reflected in the depth of charging as well. The difference in diffusivity was, however, not significant enough to explain the big differences in the size of the brittle zone for the Al-added TWIP steel compared to the other two alloys. Due to the change in brittle fracture type (guasi-cleavage versus intergranular), the critical hydrogen concentration for brittle fracture was most likely different as indicated by the dots on Figure 9-8 representing the brittle fracture depths. An additional argument is the lower hydrogen solubility in the reference 18Mn TWIP steel while still a larger brittle fracture zone was observed. Koyama et al. [367] also stated that the change in fracture mode must have affected the quantitative relationship between diffusible hydrogen concentration and fracture stress in their work. It could, therefore, be argued that the beneficial effect of aluminium on the hydrogen embrittlement sensitivity cannot be fully attributed to its effect on the SFE. Important influencing parameters are a combined high hydrogen diffusivity and solubility and the grain boundary intergranular cracking sensitivity.



Figure 9-8: Hydrogen concentration profile with depth for the charging and test time for the three TWIP steels, the dots indicate the depth of the brittle zone

The hydrogen-assisted cracks on the ND plane were further evaluated with respect to their size and amount as a function of the strain level. The SE images in Figure 9-9 illustrate the difference in crack appearance between the three TWIP steels at the intermediate engineering strain of 30%. The SE images

in Figure 9-10 illustrate the HAC appearance just beneath the fracture surface, i.e. where higher strain values were reached. The hydrogen-assisted cracks that formed on the ND surface of the tensile tested specimens were determining for the final engineering fracture strain. It is clear that at fracture, all TWIP steels studied in the present work showed an abundant presence of large HACs. The total engineering strain at fracture was, however, different for the three TWIP steels. When comparing the images in Figure 9-9 at an equal engineering strain of 30%, clear differences were observed between the alloys. The 24.5Mn TWIP steel showed many large cracks, while the 18Mn steel had a similar fraction of smaller cracks. At an engineering strain of 30%, the 1.5Al steel showed a low fraction of small cracks. The addition of manganese thus decreased the resistance of the TWIP steel to crack initiation and propagation while the addition of aluminium increased the crack initiation and propagation resistance. This observation is consistent with the large sensitivity of the 24.5Mn TWIP steel to grain boundary cracking and the enhanced grain boundary cohesion in the presence of aluminium. Grain boundary engineering, creating more special  $\Sigma^{3n}$  boundaries characterised by a low energy and therefore also a high resistance to boundary embrittlement, decreased the number of nucleation sites for hydrogen-assisted cracks and retarded further propagation of nucleated or existing cracks [403]. The resistance to grain boundary cracking is thus very important in the HE sensitivity of TWIP steels.

Koyama et al. [385] studied the size of the work hardening associated with  $\varepsilon$ -martensite transformation, deformation twinning and dynamic strain aging in TWIP steels with different carbon contents and deformation temperatures. The contribution to the work hardening rate was given by the following order:  $\varepsilon$ -martensite transformation > deformation twinning > dynamic strain aging. An increased work hardening was, however, not observed in the presence of hydrogen in this work. Although the deformation mechanisms ( $\varepsilon$ -martensite and twinning) were positively altered, the geometrical effect of the extensive crack appearance on the surface resulted in a reduction of the work hardening rate while actually an increase should have been observed. Similar conclusions were drawn in the work of Wang et al. [404] on HE of TWIP steels.



Figure 9-9: SE images of ND plane showing HACs on the different TWIP steels tensile tested until 30% engineering strain with hydrogen precharging



Figure 9-10: SE images of ND plane below the fracture surface showing HACs on the different TWIP steels tensile tested with hydrogen precharging

As a final remark, damage arrest is an important strategy to reduce HE sensitivity in TWIP steel. A small amount of ductile  $\varepsilon$ -martensite acted as a microstructural feature capable of arresting damage in binary Fe-Mn steels [146]. The hydrogen embrittlement sensitivity of Fe-32Mn was lower than other Fe-Mn-C TWIP steels due to the occurrence of the  $\varepsilon$ -martensite transformation, despite also being prone to a lot of hydrogen-assisted damage [53]. In the present work, the large fraction of  $\varepsilon$ -martensite on the surface of the 18Mn TWIP steel might also have contributed to a lower embrittlement compared to the 24.5Mn and 1.5Al TWIP steel not prone to extensive  $\varepsilon$ -martensite transformation.

# 9.3. <u>Conclusions</u>

It is generally accepted that when aluminium is added to TWIP steel, the stacking fault energy of the alloy increases. Moreover, the addition of aluminium has been stated to increase the HE resistance of TWIP steels. It was, therefore, suggested that the stacking fault energy increase might be a possible reason for the lower HE sensitivity. To verify this, an alloy with an increased manganese content was created (Fe-24.5Mn-0.6C) exhibiting a similar stacking fault energy as an Al-added TWIP steel (Fe-18Mn-0.6C-1.5Al). The HE sensitivity of both TWIP steels was compared with the performance of Fe-18Mn-0.6C TWIP steel as a reference. The following conclusions were made:

- The increase in stacking fault energy by both alloying additions (Al and Mn) resulted in a lower twin fraction and, therefore, a lower UTS value and elongation at fracture when tested in air. Moreover, aluminium addition lowered the DSA effect by its reduction of the carbon activity.
- It was experimentally confirmed that the addition of aluminium reduced the HE sensitivity in the present work after ex-situ tensile testing with a heterogeneously precharged hydrogen concentration. The alloy with an increased manganese content, however, showed a higher HE sensitivity compared to the reference alloy.
- Hydrogen lowered the stacking fault energy of all three alloys. For the Al- and Mn-added TWIP steels this resulted in an increase in the twin fraction while the reference alloy showed εmartensite transformations.
- Analysis of the fracture surfaces showed that aluminium addition promoted quasi-cleavage fracture while manganese addition promoted intergranular fracture. The Mn-added steel was much more prone to hydrogen-assisted crack initiation. Aluminium addition, however, increased the cracking resistance. A possible explanation was that aluminium had a positive effect on grain boundary cohesion (e.g. more homogeneous deformation and less carbide precipitation) while manganese reduced it.
- Based on the effective hydrogen diffusivity, which was only slightly reduced in the presence of aluminium, and the increased hydrogen solubility in the presence of aluminium, it was concluded that quasi-cleavage fracture required a higher critical hydrogen concentration than intergranular fracture. Manganese addition both increased the hydrogen diffusivity and solubility while at the same time reduced the critical hydrogen concentration to initiate fracture.

The SFE increase associated with the addition of aluminium, hence, appeared not to be determining in the present work. The grain boundary cracking sensitivity and the combination of high hydrogen diffusivity and solubility were decisive.

# Chapter 10 Conclusions and outlook for the future

### 10.1. <u>Conclusions</u>

The interaction between hydrogen and austenitic steels appeared to be a fascinating subject with multiple facets and interplaying phenomena. By focussing on three different material classes, the interaction could be studied from different perspectives. The material classes included 2205 duplex stainless steel, 304(L) austenitic stainless steel and twinning-induced plasticity steel. The main insights that were gained in this PhD are given below. The conclusions are subdivided with respect to the two sub-objectives that were formulated in Figure 1-2.

Part A: Hydrogen absorption, diffusion and trapping

- Galvanostatic electrochemical hydrogen charging was able to charge austenitic steels with
  hydrogen as was already done extensively on BCC materials. Due to the intrinsically low hydrogen
  diffusivity, this is a very slow process at room temperature making it practically impossible to reach
  a homogeneous hydrogen concentration through the thickness in a reasonable amount of time for
  a specimen with a thickness in the millimeter range. The high hydrogen concentrations that were
  introduced by charging in a sulphuric acid solution resulted in dislocation nucleation and migration
  although no external stress was applied. The observed plastic deformation was a result of the
  reduction in the shear modulus by hydrogen combined with internal stresses and stresses applied
  on the lattice by hydrogen. The interaction of hydrogen with dislocation nucleation and propagation
  is generally of major importance in metals (BCC, FCC, HCP, ...), cf. the HELP mechanism.
- The analysis of experimental TDS data for austenitic steels was addressed. It was shown that for materials characterised by a low hydrogen diffusivity, the rate-determining step for hydrogen desorption during a TDS experiment was interstitial diffusion rather than hydrogen detrapping. Heterogeneous hydrogen charging resulted in peak splitting during desorption. These peaks were falsely identified as hydrogen trapping sites in a lot of literature while they actually represent concentration gradient-driven hydrogen diffusion towards the surface and the specimen center. The peak splitting was observed for the fully austenitic steels studied in this PhD as well as for the duplex stainless steel containing only 53% of austenite. The effective hydrogen diffusion was sufficiently low in this steel type to be the rate-determining step. Therefore, it was clearly illustrated that TDS evaluation of low diffusion materials should be executed and analysed carefully.
- TDS can be used as an alternative technique to evaluate the effective hydrogen diffusion coefficient and hydrogen solubility of austenitic materials when combined with numerical diffusion modelling. In literature, gas phase high temperature permeation experiments were used, however, limited data is available. The TDS technique can be used on materials that contain a heterogeneous hydrogen concentration through the thickness which was in particular interesting for room temperature electrochemical hydrogen charged specimens. Moreover, TDS data of materials other than FCC steels that are characterised by a low hydrogen diffusivity, could be analysed with the developed models in this PhD, e.g., titanium alloys with a large fraction of HCP a phase or FCC nickel alloys.
- The effective hydrogen diffusion coefficients of the three investigated TWIP steels were higher than
  those of 304L austenitic stainless steel with and without prestraining as summarised in Figure 10-1.
  The values were evaluated from the temperature-dependent equations for the effective diffusivity
  at 298K obtained through TDS. This indicates that although the lattice was similar (FCC), the
  chemical composition had a noticeable influence on the free space between the atoms influencing
  interstitial hydrogen diffusion. Comparison of the hydrogen solubility was not possible in this PhD

due to the use of an alternative electrolyte for the TWIP study. The system was governed by a different equilibrium surface concentration.



## Figure 10-1: Effective hydrogen diffusion coefficient at room temperature (298 K) for different fully austenitic steel types investigated in this PhD

Part B: Mechanical properties and deformation mechanisms

- Hydrogen influenced the deformation processes during straining. Its presence made dislocation
  motion more planar. Similar observations were done in FCC aluminium. Moreover, hydrogen was
  found to decrease both the stacking fault energy and the austenite stability resulting in enhanced
  deformation twinning and/or martensitic transformation. The chemical composition of the
  investigated materials determined the preferred mechanism. The austenite fraction of the DSS
  preferentially transformed to ε-martensite under the influence of hydrogen. For 304L ASS, the α'martensitic transformation was enhanced while also ε-martensite appeared. For the TWIP steels
  exhibiting a rather high initial SFE (Fe-18Mn-0.6C-1.5Al and Fe-24.5Mn-0.6C TWIP steel), twinning
  was enhanced while for the TWIP steel with low initial SFE (Fe-18Mn-0.6), ε-martensite was
  observed.
- All studied alloys were prone to hydrogen-assisted cracking at the surface. The resistance to hydrogen-assisted cracking determined to a large extent the HE susceptibility of the investigated austenitic steels. The DSS showed preferential crack initiation in the austenite phase fraction due to the high hydrogen concentrations leading to many stress concentrations within the grains. It was concluded that crack initiation was not directly related to the formation of ε-martensite.
- Prestraining increased the sensitivity to hydrogen embrittlement for metastable 304L ASS due to the formation of defects and a'-martensite characterised by a high hydrogen diffusivity. The increased defect concentration after prestraining resulted in a larger susceptibility to crack initiation and propagation. An increased defect concentration only at the surface sufficed to decrease the obtainable elongation at fracture.
- In high-manganese TWIP steels, grain boundaries were prone to hydrogen-assisted crack initiation
  and propagation, which was never observed in the stainless steel types where quasi-cleavage
  fracture was present. For materials prone to intergranular cracking, the grain boundary cohesive
  strength was of major importance. It was positively influenced by the addition of aluminium while
  an increase in the manganese fraction decrease it. The HE sensitivity changed accordingly. Due to
  the crucial importance of the grain boundary cracking, the role of the stacking fault energy could

not be determined. Intergranular cracking in the presence of hydrogen also often occurs in nickel alloys and along prior austenite grain boundaries in martensitic steels.

- Within the study of 304L ASS, it was shown that the applied crosshead displacement rate influenced the size of the hydrogen effect. This was linked to the time that was given for hydrogen to diffuse, similarly as for BCC steel types and other FCC or HCP materials. Due to the metastability of the 304L austenite matrix towards the transformation to a'-martensite, the effective hydrogen diffusivity continuously increased during the tensile tests.
- Finally, the chemical composition was of major importance in the hydrogen embrittlement sensitivity of the studied austenitic steels. It determined the stacking fault energy and austenite stability and as a consequence also the operational deformation mechanisms. Moreover, it influenced the hydrogen solubility and diffusivity and grain boundary cohesive strength, all of which are important parameters in the HE sensitivity of (austenitic) steels and metals in general.

## Conclusions and future work

# 10.2. <u>Suggestions for future work</u>

The need for hydrogen-resistant materials to accomplish the transition to a hydrogen economy remains. At the same time, the governing mechanisms of the hydrogen embrittlement phenomenon are still under debate. A lot of research is, therefore, still conducted and dedicated conferences are held indicating the importance of the subject. Below, several suggestions for future research are given based on the performed research on austenite-containing steels in this PhD.

- A lot of progress could be made with more standardised experimental procedures. The current literature contains a lot of interesting data which cannot be compared with certainty to one another because of the different research approaches. The differences (or similarities) between gaseous charging and electrochemical hydrogen charging should for example be elucidated.
- Research in the present work mainly focussed on heterogeneously, electrochemically hydrogen charged specimens containing high hydrogen concentrations. The gained insights should also be validated for homogeneously charged specimens and specimens containing lower hydrogen concentrations. Although the effects are expected to be less pronounced with lower hydrogen concentrations, the intrinsic effect of hydrogen on deformation and fracture is expected to be similar.
- In this PhD, the bulk hydrogen properties of austenitic steels were addressed. The surface state, however, largely influences the hydrogen absorption kinetics. Specific oxide layers can for example act as barriers for hydrogen entry increasing the hydrogen embrittlement resistance. Several (advanced) surface characterisation techniques could be applied to characterise the surface oxide layers on austenitic steels such as wavelength dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and Auger electron spectroscopy. The latter two allow the investigation of the top few nm of a metal. The entry and release of hydrogen could also be monitored by various electrochemical characterisation methods. Macroscopically, cyclic voltammetry could monitor the hydrogen uptake and release. Locally, scanning Kelvin probe force microscopy could be used allowing the visualisation of hydrogen in the microstructure by a change in the work function. Secondly, the cyclic voltammetry method could be used in a micro-capillary cell.
- The proposed numerical diffusion model was able to fit the experimental TDS data in a reliable way. Microstructure-based hydrogen diffusion and trapping models could, however, lead to a major step forward for the simulation of TDS data. Especially for materials containing more than one phase with a different diffusivity, such as the duplex stainless steels studied in this work, or materials containing precipitates or inclusions with a detrapping activation energy close to or higher than the diffusion activation energy, this could create a large added value to the TDS analysis.
- Micro-mechanical tensile testing inside a SEM chamber could be performed to assess crack
  initiation and propagation in a controlled manner. As such, the exact moment of crack initiation
  could be visualised through video recording allowing this parameter to be used as a ductility
  measure as well. Throughout this PhD, crack initiation and propagation appeared to be of major
  importance for the hydrogen embrittlement sensitivity. Since the tests are performed inside the
  SEM chamber, only precharged specimens can be tested. It was shown, however, that ex-situ
  tensile testing can lead to significant embrittlement with limited hydrogen losses in austenitic
  steels due to the intrinsic low hydrogen diffusivity. By pausing the tensile test at selected strain
  levels, detailed SEM/EBSD analyses can be performed immediately. The electron channeling
  contrast imaging technique could additionally be a major improvement since this technique is
  able to directly observe lattice defects such as dislocations and stacking faults close to the

surface of bulk specimens. This would allow an in-depth comparison of the differences in deformation mechanisms with and without hydrogen pre-charging.

- A more in-depth characterisation of the grain boundary characteristics, relevant for example for the three investigated TWIP steels, could give valuable information on how to improve the resistance to grain boundary cracking in the presence of hydrogen. Due to the limited corrosion resistance of the TWIP steels, electrochemical polishing to create TEM foils appeared not a suitable procedure for TEM observation. Focussed ion beam (FIB) could be used to prepare a TEM slice with a grain boundary included, which could then be subjected to EDX and diffraction measurements (for carbide identification) in the TEM. Some of the hypotheses that were discussed in chapter 9 based on literature observations could as such also be confirmed experimentally. Moreover, the FIB technique could in general be useful for careful selection of TEM slices at specific locations. As a large hydrogen concentration gradient was present from the surface onwards, the microstructural characteristics of the TEM slice betained at a certain location within the hydrogen-affected zone could be linked more precisely to a certain hydrogen concentration. FIB could also be used to create TEM slices just beneath or at the fracture surface enabling the evaluation of the fracture mechanism.
- Finally, major research efforts are required for the potential strengthening effect of hydrogen. Since hydrogen was clearly able to enhance (nano)twinning and martensitic transformations, an increase in work hardening in the presence of hydrogen could be within reach. Tuning chemical compositions and microstructures towards these features might result in material solutions with enhanced hydrogen embrittlement resistance. Especially nanotwin formation and ε-martensite formation possess major potential for improved HE resistance or even an increased ductility in the presence of hydrogen. The influence of additive manufacturing, a fabrication technique that has gained a lot of interest recently, on the microstructure and hydrogen embrittlement resistance should also be evaluated in more depth since promising results were already obtained.

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