

6th WMRI Early Career Scientist Summit, NPL Teddington UK, 18-22 June 2018

*HYDROGEN ASSISTED CRACKING PHENOMENA
IN DUPLEX STAINLESS STEELS
ELUCIDATED BY IN- AND EX-SITU TOF-SIMS EXPERIMENTS*

Oded Sobol

Oded.Sobol@bam.de

www.bam.de

OUTLINE



Introduction

- Hydrogen assisted cracking in offshore applications
- Hydrogen sensitive methods in the microscale

Experimental Approaches

- Types of experiments

Results and Discussion

- Ex-situ observations and data fusion
- In-situ permeation and mechanical loading

Conclusions

INTRODUCTION

HYDROGEN ASSISTED CRACKING IN OFFSHORE APPLICATIONS



[<https://www.ogdaily.com>]



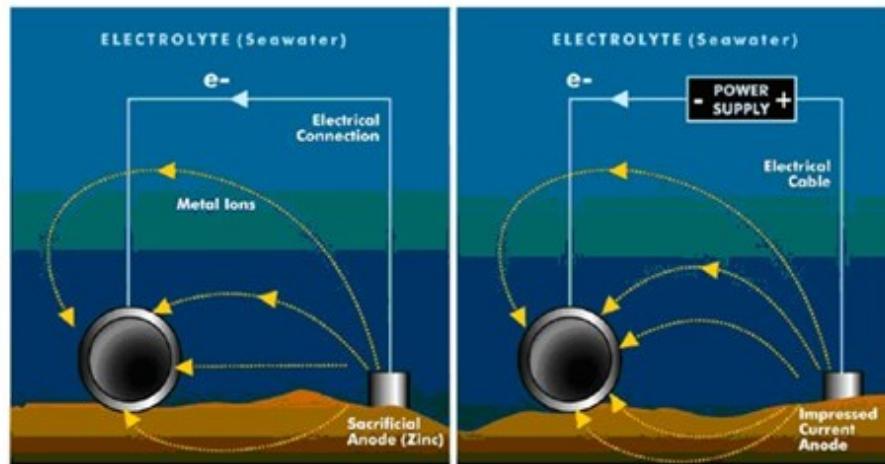
[IMOA, London, UK, 2014]

INTRODUCTION

HYDROGEN ASSISTED CRACKING IN OFFSHORE APPLICATIONS



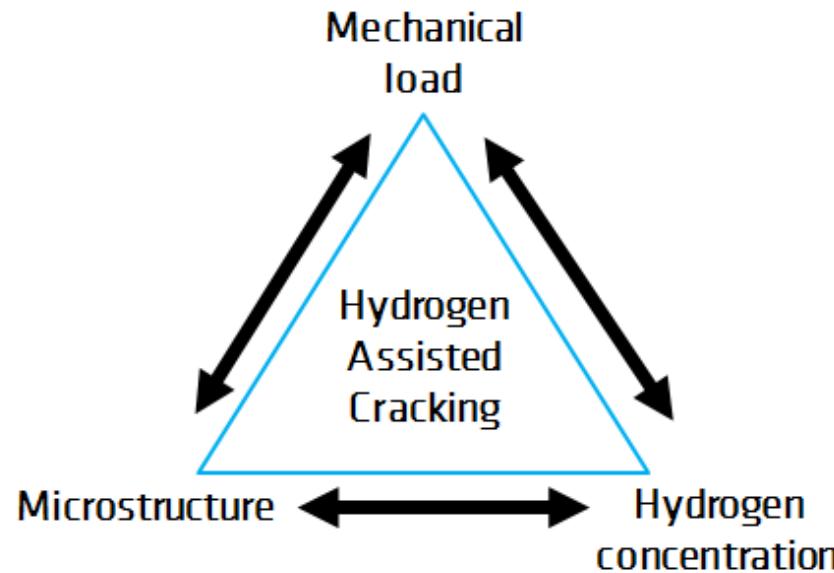
[<https://www.ogdaily.com>]



INTRODUCTION

HYDROGEN ASSISTED CRACKING AND DEGRADATION

- HAC: well known for more than 150 years
- HAC related degradation of the properties more in terms of ductility than in strength
- Real metallurgical mechanisms have not yet been clarified
- General agreement: HAC cannot be explained by a single mechanism



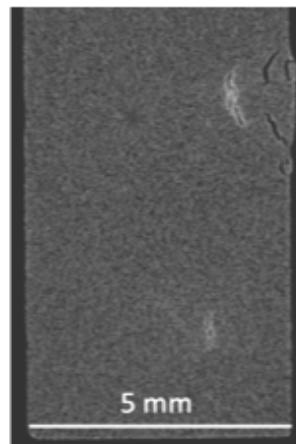
- Theories and models validation by macroscale H-sensitive methods and microscale observations by indirect methods
- Microscale H-sensitive methods are required

INTRODUCTION



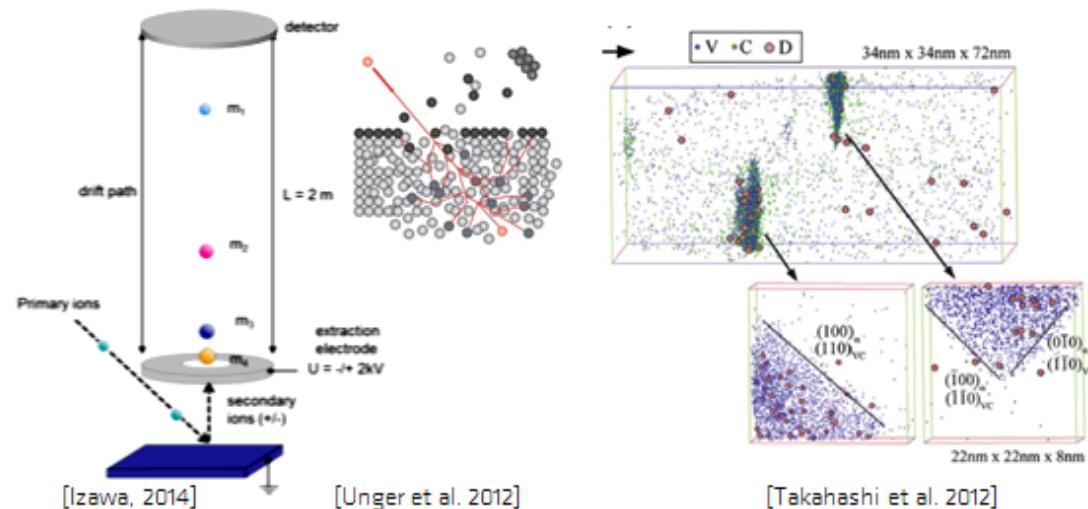
HYDROGEN SENSITIVE METHODS IN THE MICROSCALE

- Very few direct approaches to image the hydrogen distribution in the microstructure



[Griesche et al. 2014]

Neutron tomography: $10^1 \mu\text{m}$



[Unger et al. 2012]

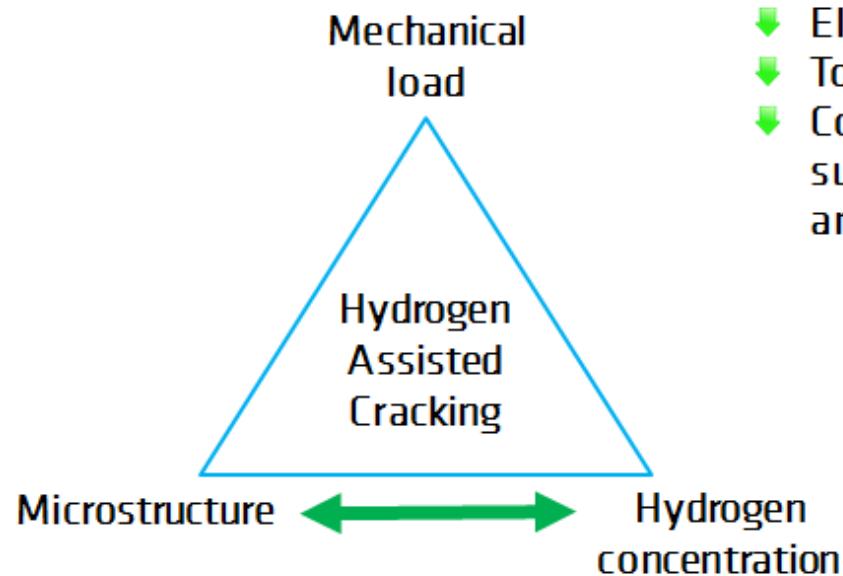
ToF-SIMS: $10^{-2} \mu\text{m}$

[Takahashi et al. 2012]

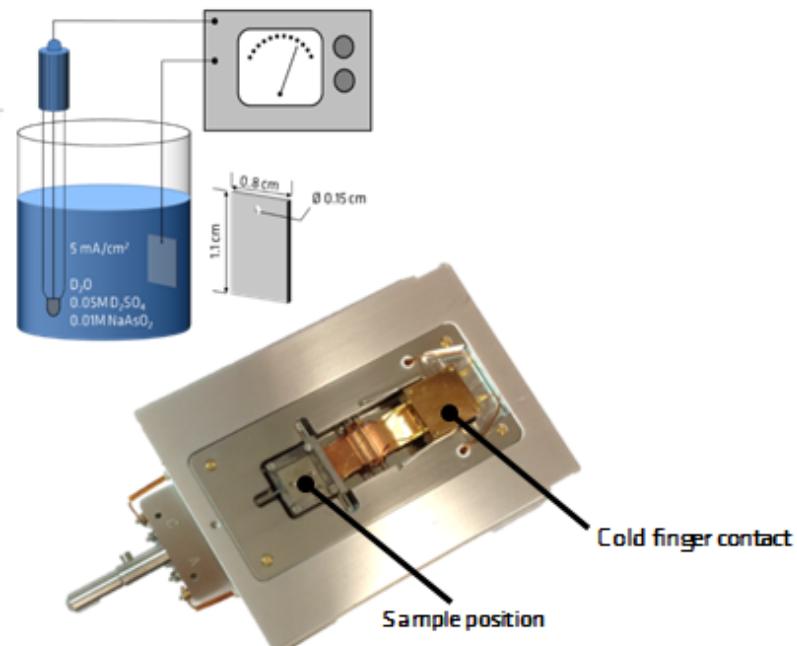
Atom-probe tomography: $10^{-4} \mu\text{m}$

- The better the spatial resolution, the more complicated the sample preparation and experimental setup become.
- Deuterium ($\text{D}, {}^2\text{H}$) is mostly used as a tracer for hydrogen (H)

TYPES OF EXPERIMENTS



- ▼ Electrochemical charging
- ▼ ToF-SIMS analyses for chemical distribution
- ▼ Comprehensive investigations by supplementary techniques (for structural and microstructural characterization)

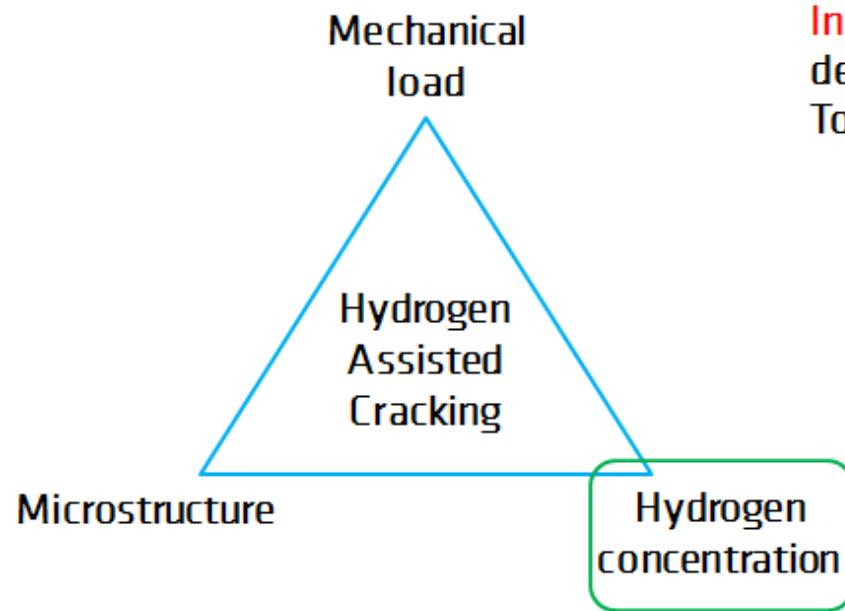


Supplementary techniques:

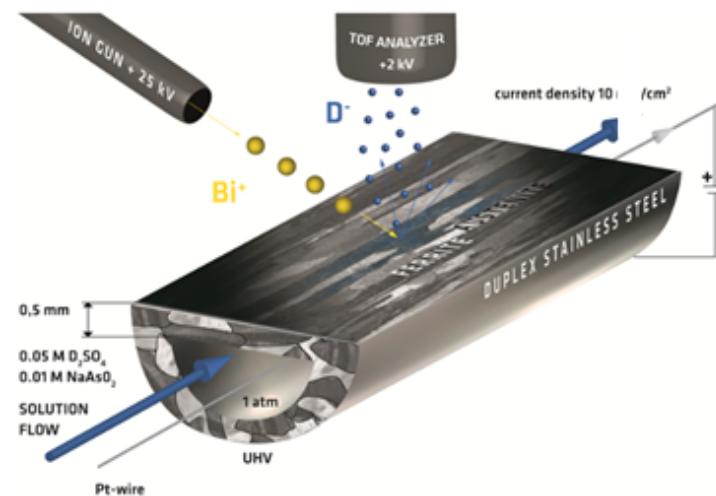
- HR-SEM: microstructure characterization
- EBSD: structural characterization
- FIB: cross-section preparation

Use of deuterium (D , ${}^2\text{H}$) as a tracer for hydrogen (H)

TYPES OF EXPERIMENTS



In-situ electrochemical permeation of deuterium through the microstructure during ToF-SIMS analyses for chemical distribution

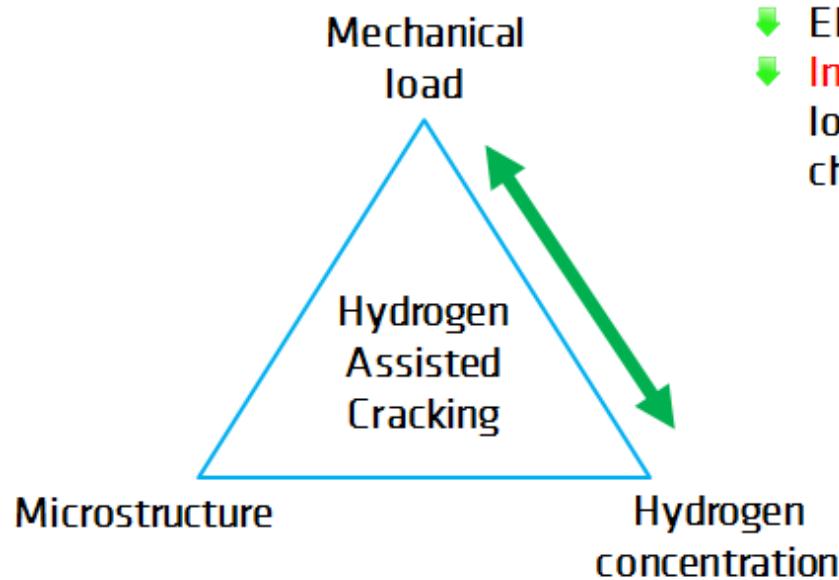


Supplementary techniques:

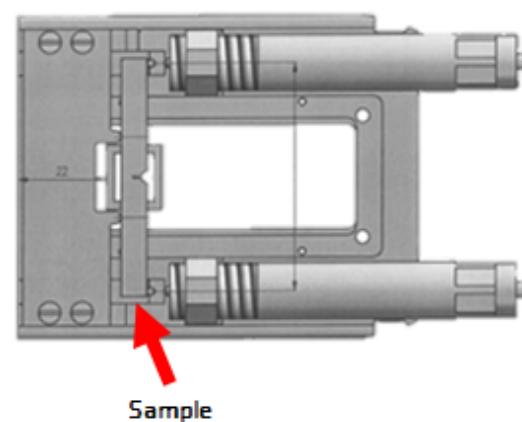
- HR-SEM: microstructure characterization
- EBSD: structural characterization
- FIB: cross-section preparation

Use of deuterium (D, ²H) as a tracer for hydrogen (H)

TYPES OF EXPERIMENTS



- ▼ Electrochemical charging
- ▼ In-situ ToF-SIMS analyses **during** mechanical load for monitoring the change in the chemical distribution



Supplementary techniques:

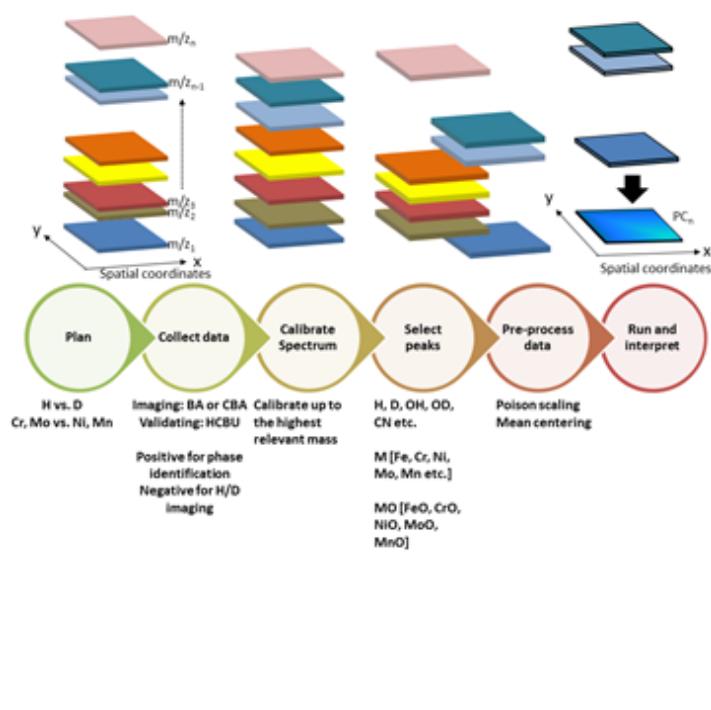
- HR-SEM: microstructure characterization
- EBSD: structural characterization
- FIB: cross-section preparation

Use of deuterium (D , 2H) as a tracer for hydrogen (H)

EXPERIMENTAL APPROACHES

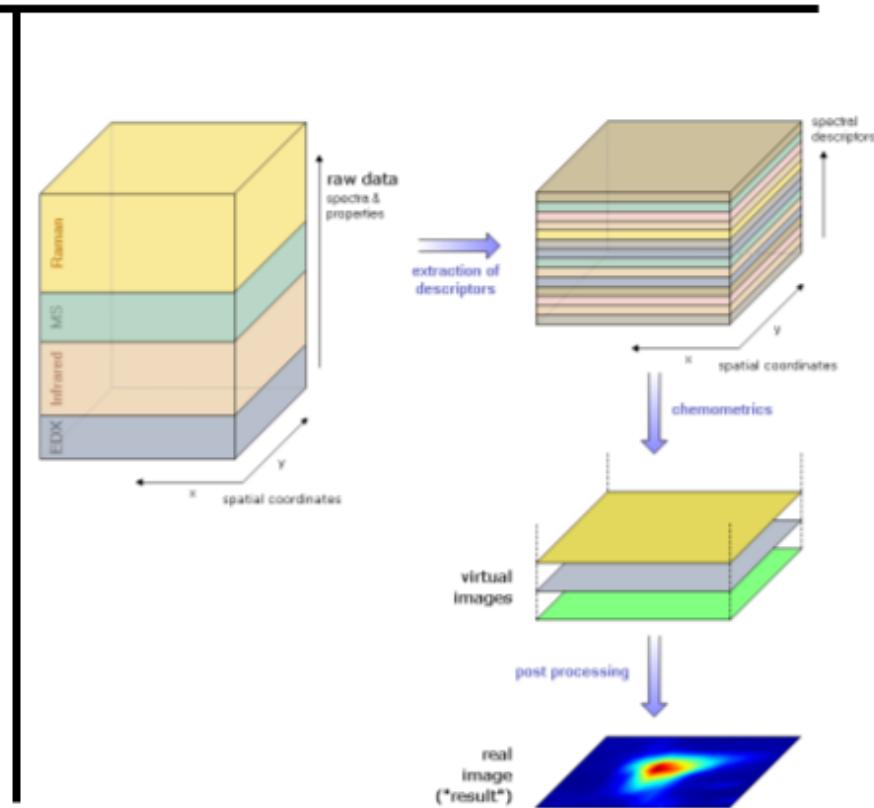
DATA POST-PROCESSING AND DATA FUSION

Multivariate data analysis by principal component analysis (PCA)



[Sobol et al. 2018]

Data fusion

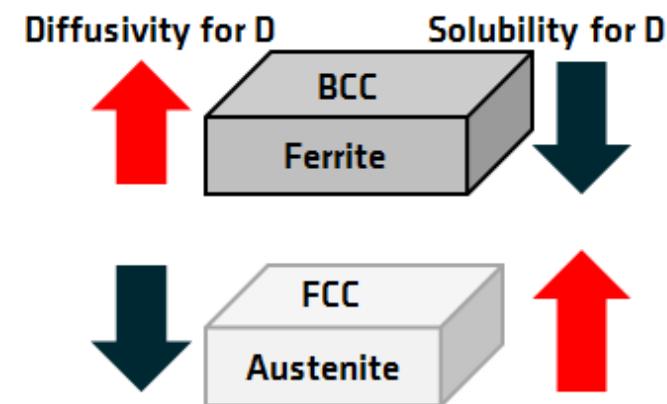
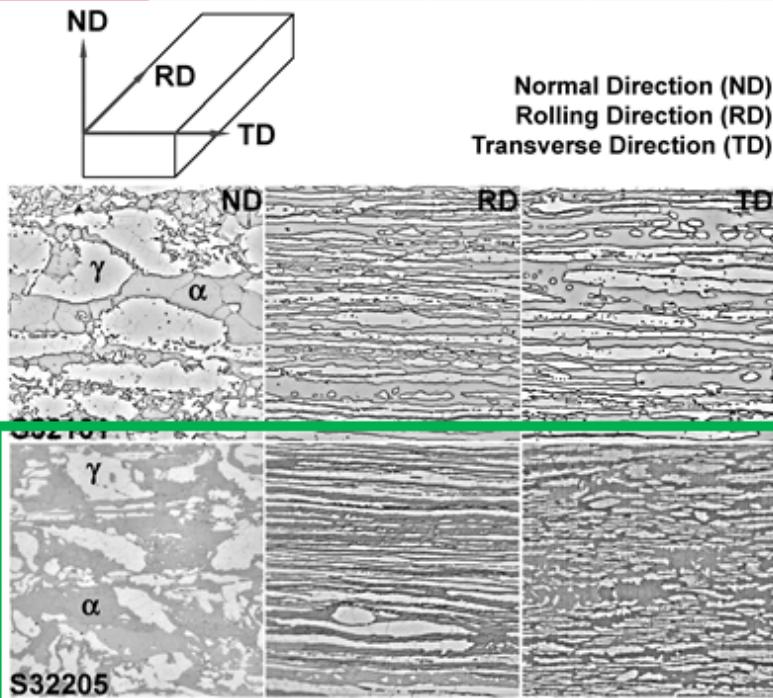


[Lohninger et al. 2014]

TESTED MATERIALS

STANDARD AND LEAN DUPLEX STAINLESS STEEL

Steeltype	Fe	Cr	Ni	Mo	Mn	Si	C	N
DSS 2205	Bal.	22.0-23.0	4.5-6.5	3.0-3.5	2.0 max	1.0 max	0.03 max	0.14-0.20
LDX 2101	Bal.	21.0-22.0	1.35-1.7	0.1-0.8	4.0-6.0	1.0 max	0.04 max	0.20-0.25



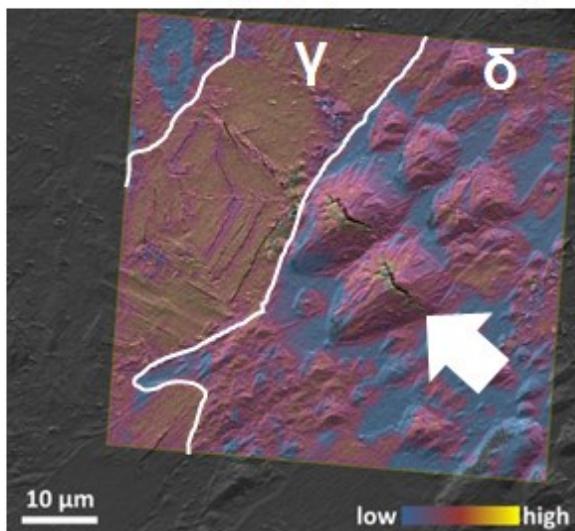
Results I:

Ex-situ SIMS/SEM/EBSD experiments

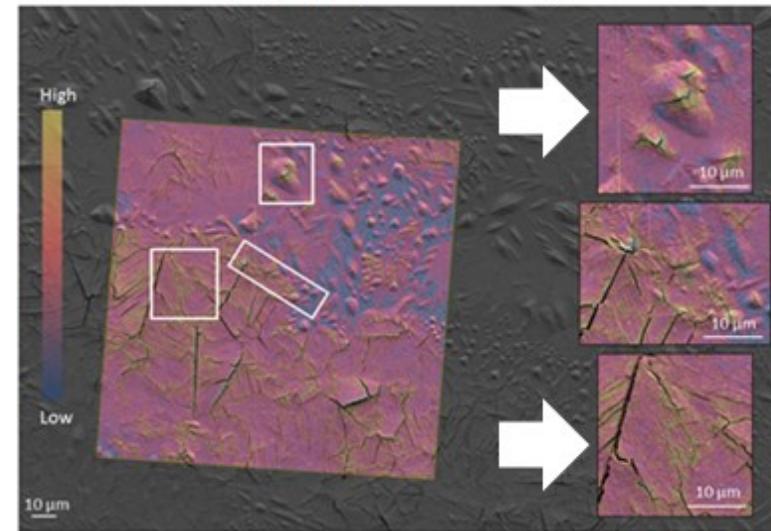
RESULTS

DSS 2205: Ex-situ analyses and data fusion

ToF-SIMS topography fusion image



ToF-SIMS topography fusion image

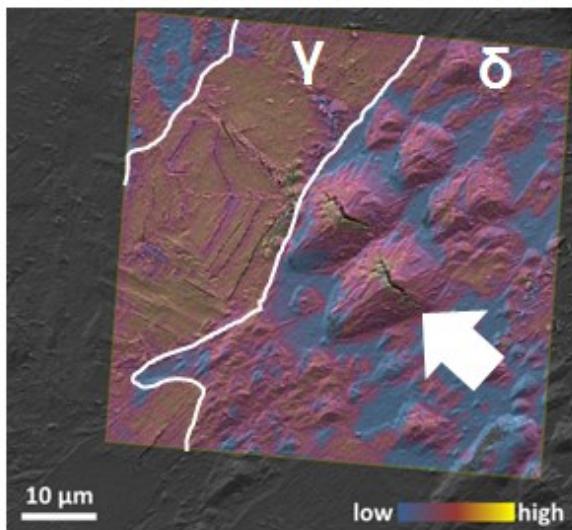


- Differences in deuterium concentration between ferrite [δ] and austenite [γ]
- Blisters in the ferrite, parallel cracking in the austenite
- Enhanced deuterium concentration at highly deformed regions (blisters, cracks, interfaces).
- The formation of blisters in the ferrite originates at the δ - γ interface

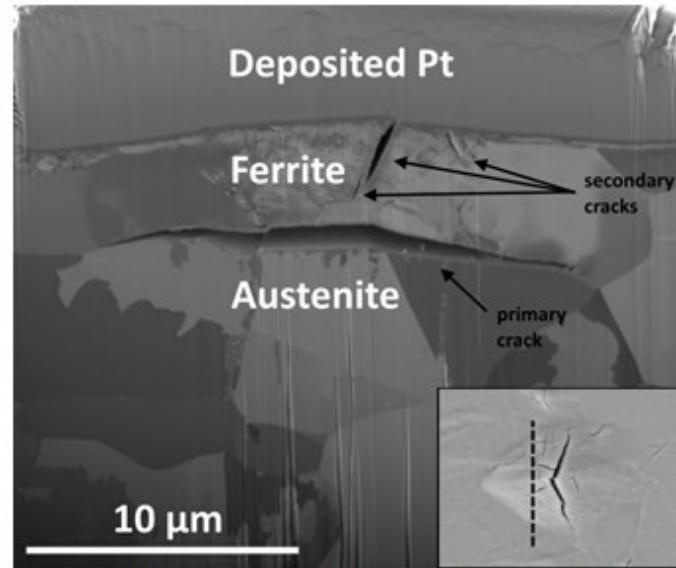
RESULTS

DSS 2205: Ex-situ analyses and data fusion

ToF-SIMS topography fusion image



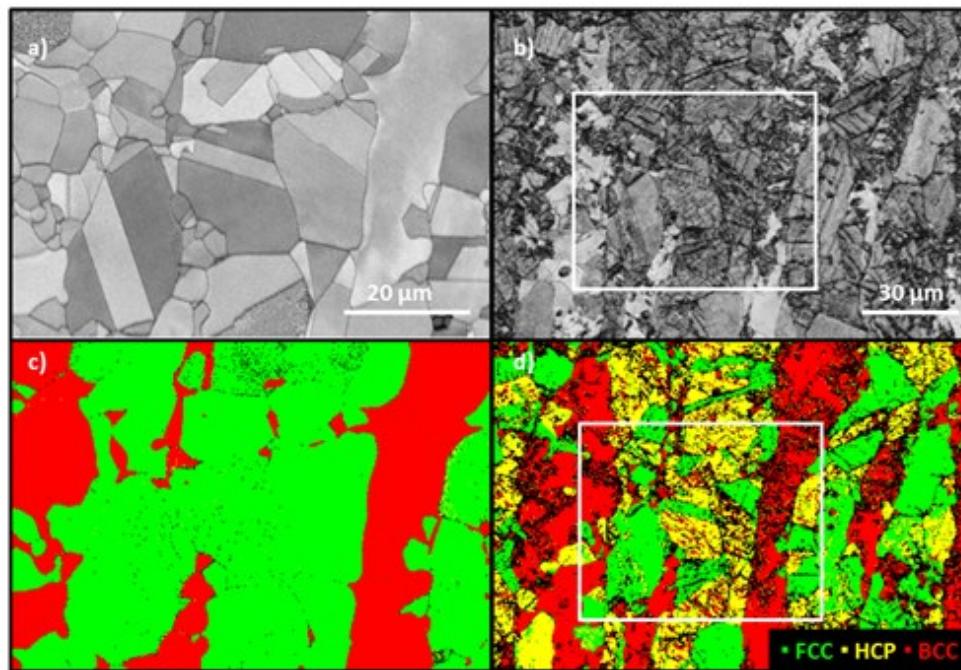
FIB cross section



- Differences in deuterium concentration between ferrite [δ] and austenite [γ]
- Blisters in the ferrite, parallel cracking in the austenite
- Enhanced deuterium concentration at highly deformed regions (blisters, cracks, interfaces).
- The formation of blisters in the ferrite originates at the δ - γ interface

RESULTS

PHASE TRANSFORMATION OF THE AUSTENITIC PHASE – DSS2205



- γ in DSS 2205: HCP phase and parallel cracks



Results II:

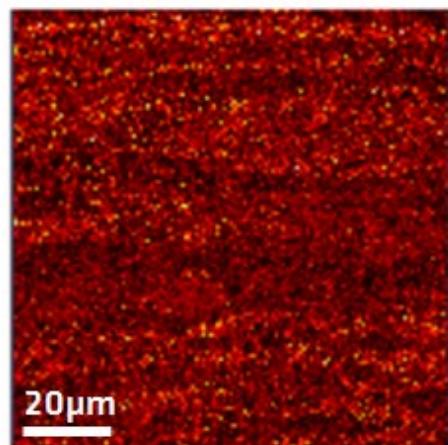
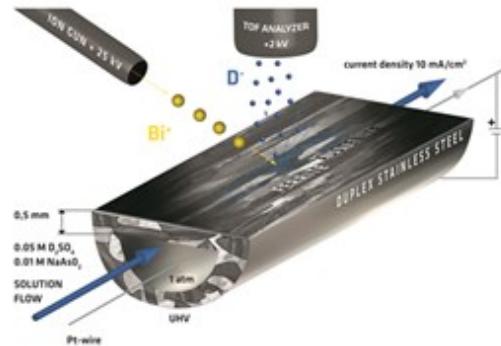
In-situ ToF-SIMS experiments

- Permeation
- Mechanical loading

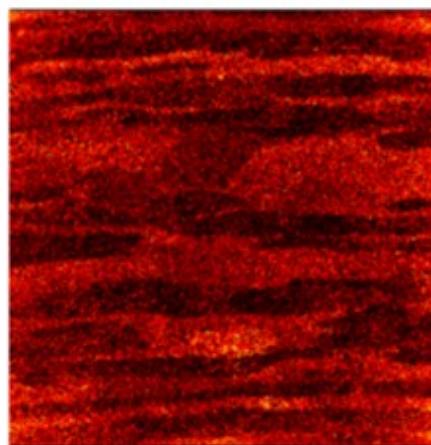
RESULTS

DSS 2205: IN-SITU PERMEATION

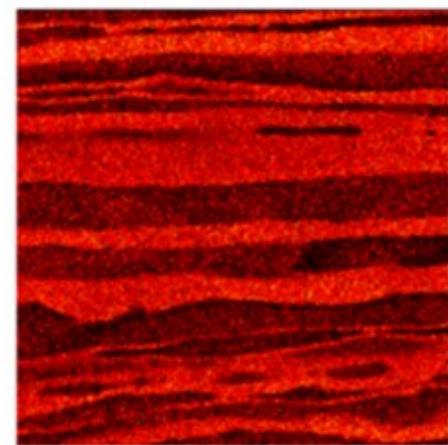
-SIMS, D⁻ detection



28 days



34 days

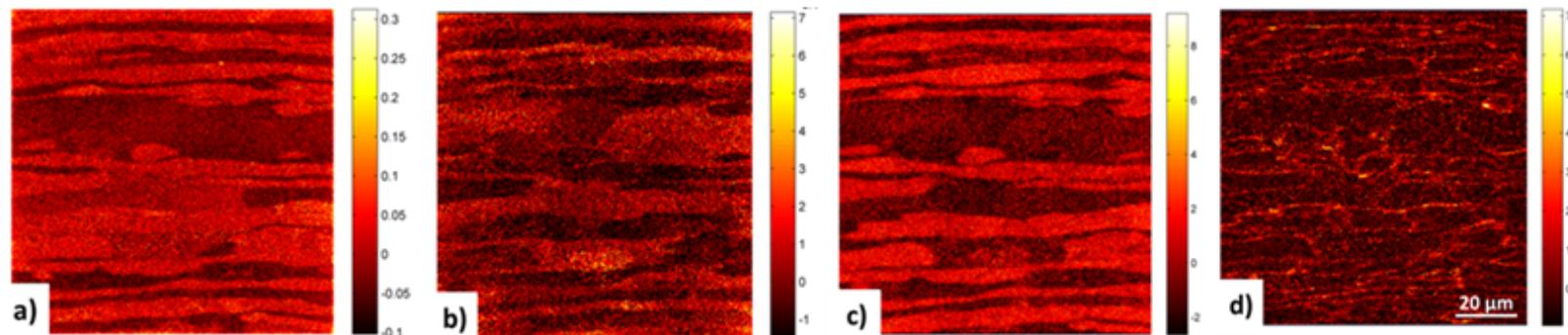


37 days (other location)

- Bright regions: deuterium indicating larger concentrations in the ferrite.
- Evidently demonstrates that the ferrite is fast diffusion path.

RESULTS

DSS 2205: IN-SITU PERMEATION



+SIMS: PC1,
Data set with all
matrix related SI

Ferrite: dark
Austenite: bright

-SIMS: PC1
Data set with all
negative SI
High PC1 loadings
for D⁻ and DO⁻
(34 days)

Ferrite: bright
Austenite: dark

-SIMS: PC1
Data set:
20 to 50 m/z only
High PC1 loading
for CN⁻

Austenite: bright

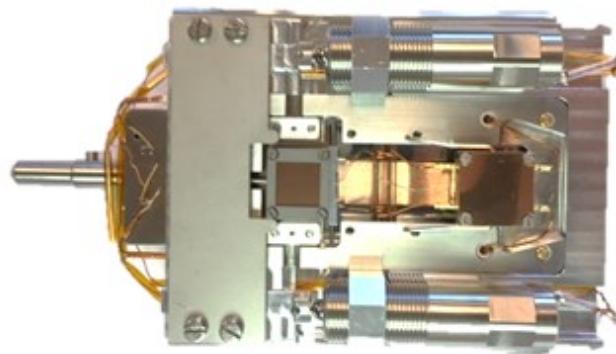
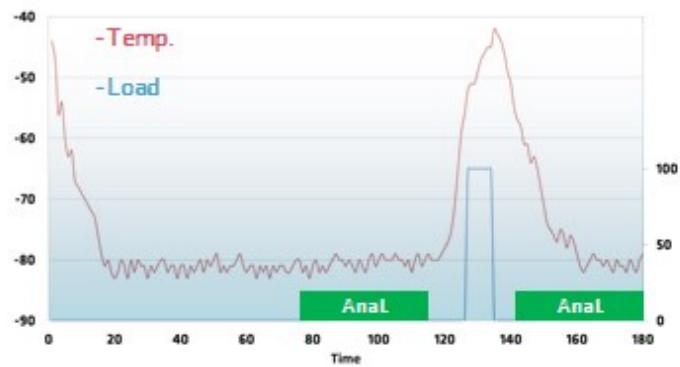
-SIMS: PC2
Data set:
20 to 50 m/z only
High PC2 loading
for CN₂HD⁻

Bright: Aust./Fer.
interfaces

RESULTS

DSS 2205: IN-SITU MECHANICAL LOADING

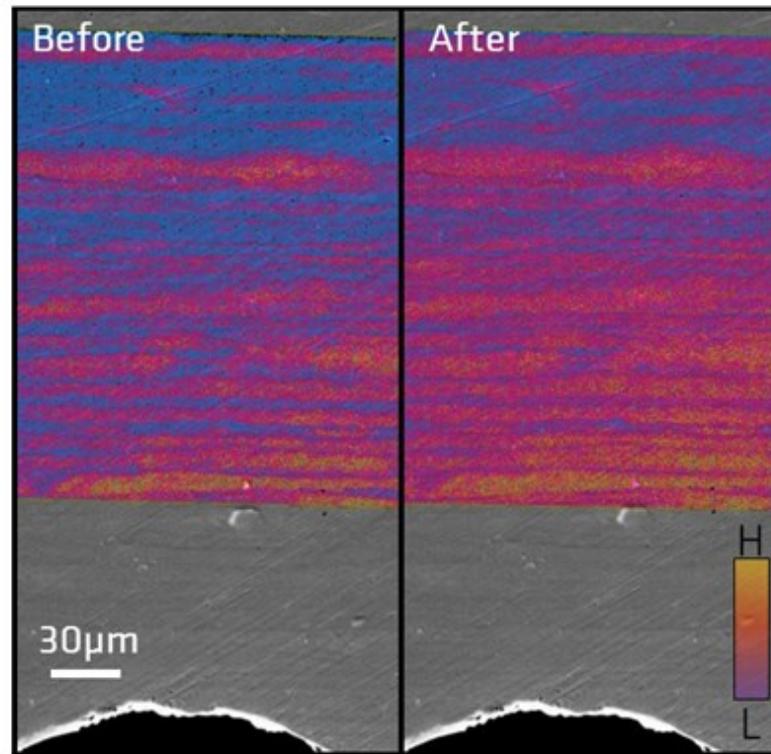
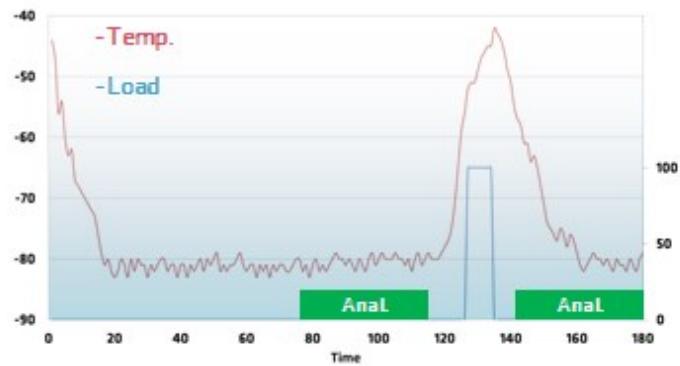
- ↓ Initial cooling
- ↓ Imaging the initial state
- ↓ Applying maximal load above the ductile-brittle transition temp. (DBTT)
- ↓ Imaging at low temperature



RESULTS

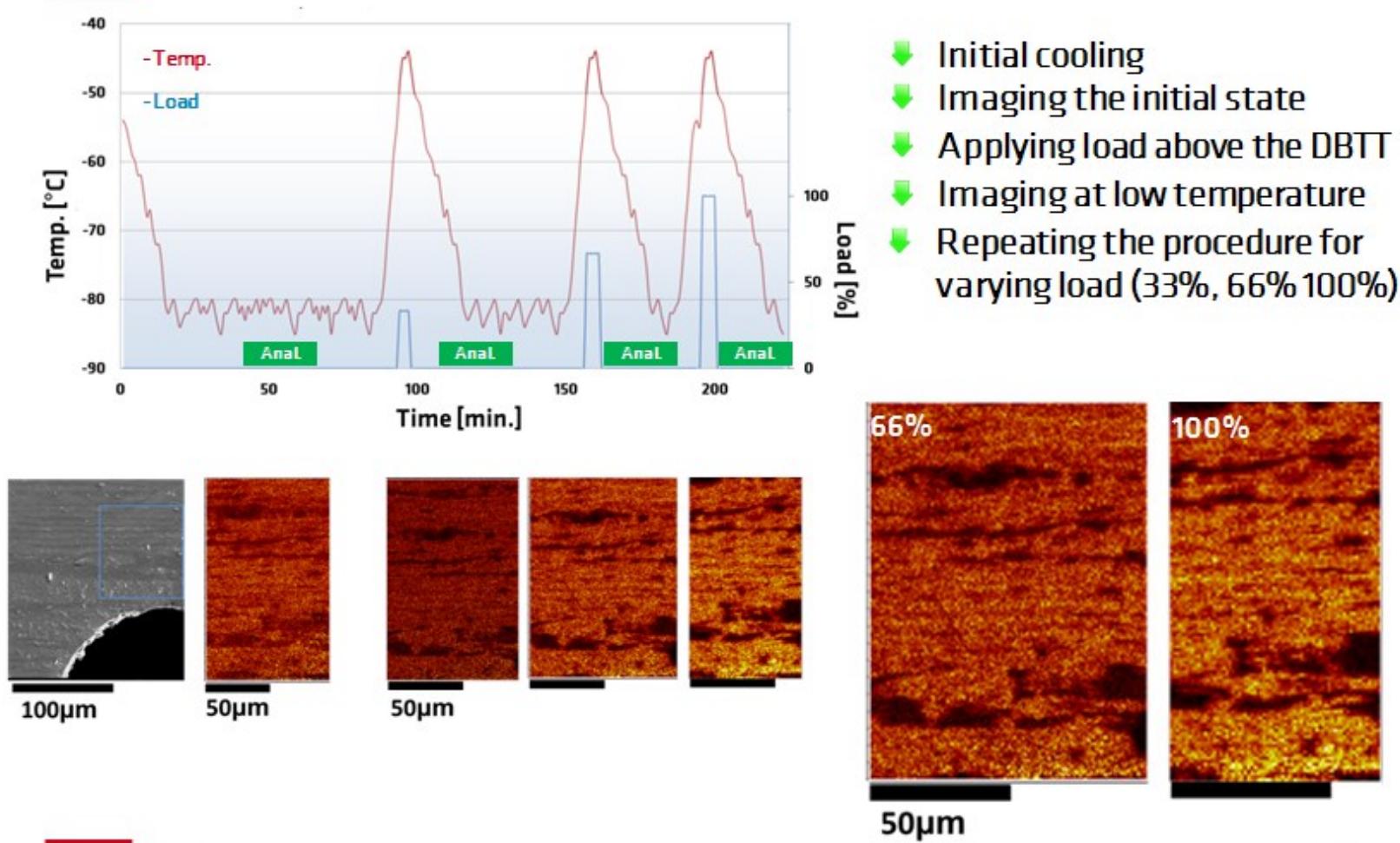
DSS 2205: IN-SITU MECHANICAL LOADING

- ↓ Initial cooling
- ↓ Imaging the initial state
- ↓ Applying maximal load above the ductile-brittle transition temp. (DBTT)
- ↓ Imaging at low temperature



RESULTS

DSS 2205: IN-SITU MECHANICAL LOADING

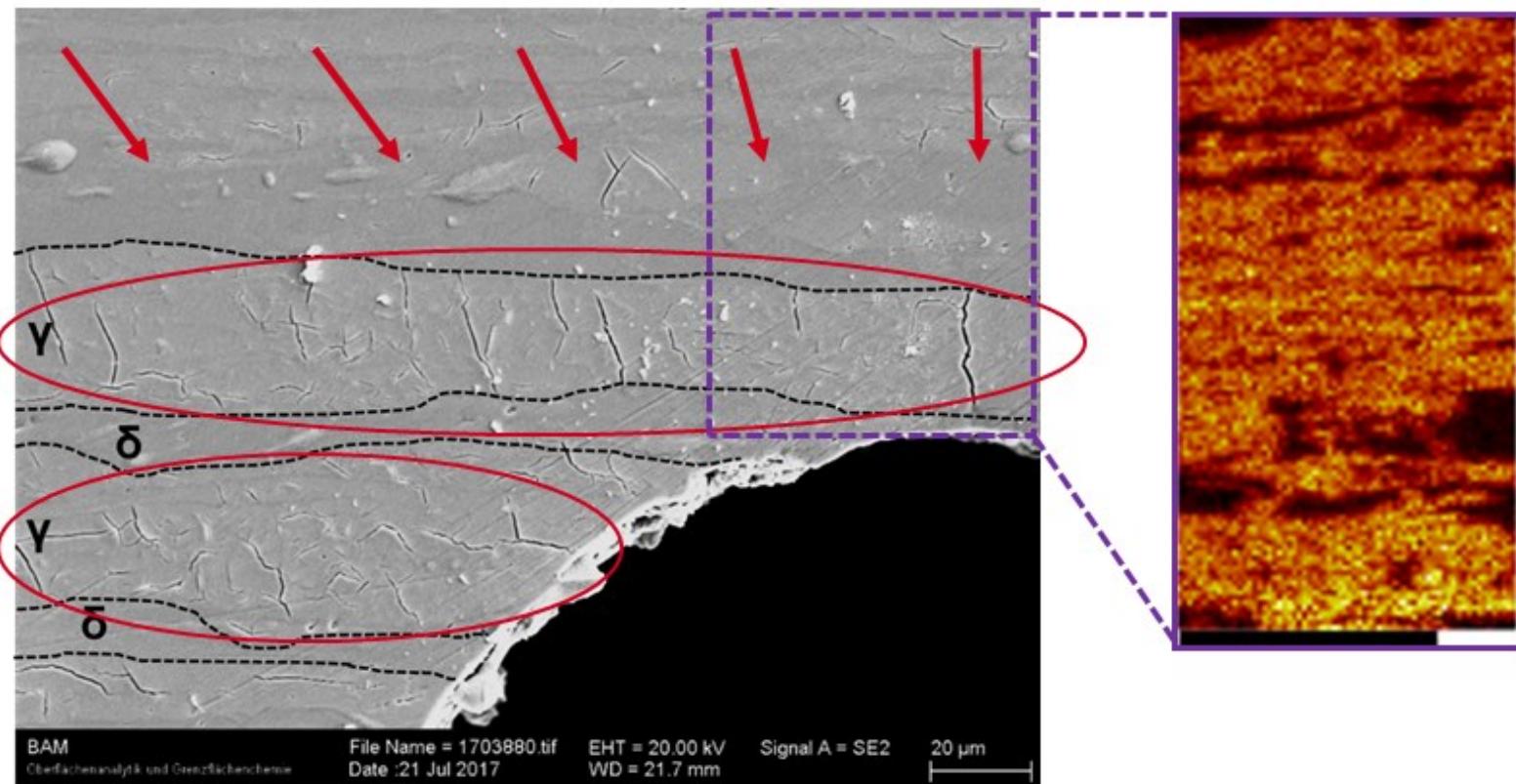


[Sobol et al. 2018]

RESULTS

IN-SITU MECHANICAL LOADING

- Brittle austenite
- Crack orientation



CONCLUSIONS



- Blistering in the ferrite can be explained by the trapping of deuterium at the interface
- Significant brittle cracking of the austenitic phase can be explained by extensive twinning and martensitic phase transformation
- Uptake of deuterium around cracks at the surface might occur due to the deformation of the microstructure in both phases
- Locally strain enhanced accumulation of deuterium (in-situ mechanical loading)
- Iteration of the loading process allows more deuterium to be transported into regions of high strains (in front of the notch)

6th WMRIF Early Career Scientist Summit, NPL Teddington UK, 18-22 June 2018

Special thanks to:

Wolfgang Unger

Dan Eliezer

Thomas Böllinghaus

Gert Nolze

Michael Rhode

Tobias Mente

THANK YOU FOR YOUR ATTENTION
