한국원자력학회
2021 추계학술발표회

Hydride Embrittlement Analysis on the End Cap Welded Zone and Heat Affected Zone of Zr-Nb alloy tube

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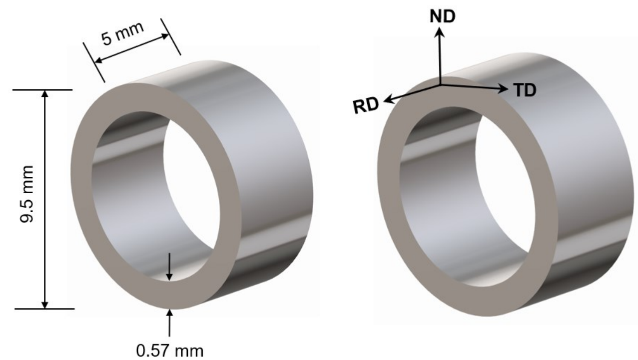
KOREAN NUCLEAR SOCIETY
2021 AUTUMN MEETING

Contents

Introduction: Previous Study on the Hydride Embrittlement

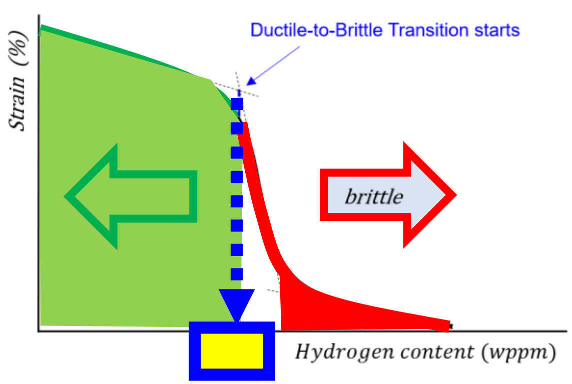
Materials : Reactor-grade Zircaloy tube

Element	Sn (%)	Fe (%)	Cr (%)	Ni (%)	O (%)	Hf	Zr	Nb (%)
Zircaloy-4	1.2~1.7	0.18~0.24	0.07~0.13	-	0.12	<100 ppm	bal.	-
Zr-Nb alloy	0~0.99	0.11	-	-	0.11	40 ppm	bal.	0.98

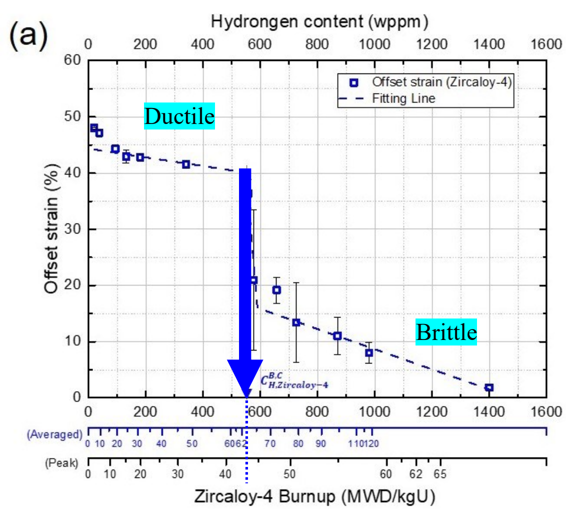


Outer diameter : 9.5mm
Thickness : 0.57mm
Length : 5mm

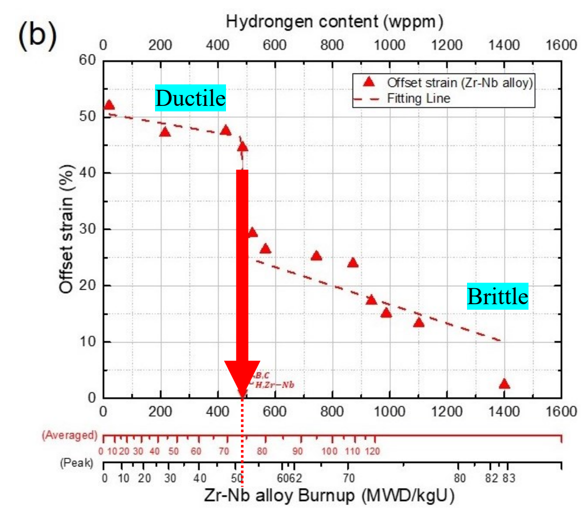
RCT test result: **Abrupt Ductile-to-Brittle Transition**



Schematic of DTB transition concept



Abrupt DTB transition happens at in Zircaloy-4

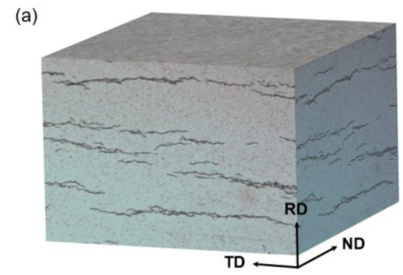


Abrupt DTB transition happens at in Zr-Nb alloy

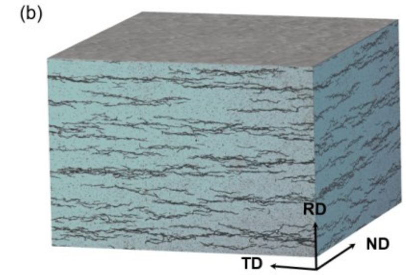
*Hydrogen concentration(wppm) and fuel Burn-up Effect(MWd/kgU) relations were obtained by FRAPCON 4.0 simulation

Introduction: Previous Study on the Hydride Embrittlement

- The DTB transition is known to occur when there is a sufficiently large number of hydrides for a crack to cross the hydrides and propagate in the matrix.



LOW Hydride connectivity (200wppm)

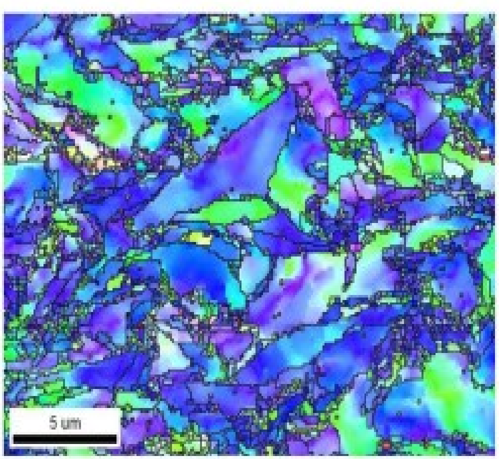


HIGH Hydride connectivity (600wppm)

- EBSD Analysis

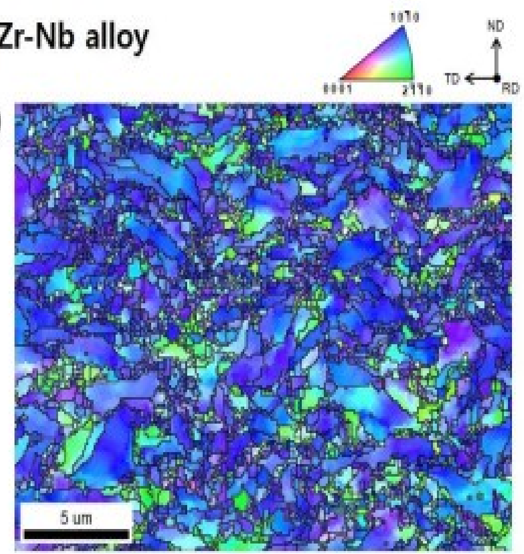
(1) Zircaloy-4

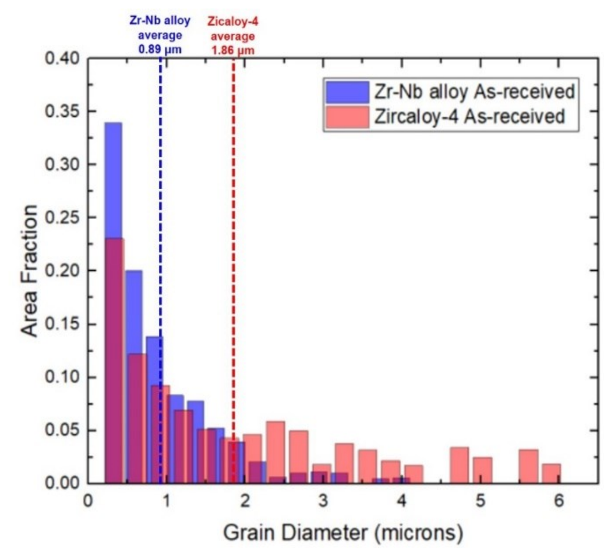
(a1)



(2) Zr-Nb alloy

(a2)



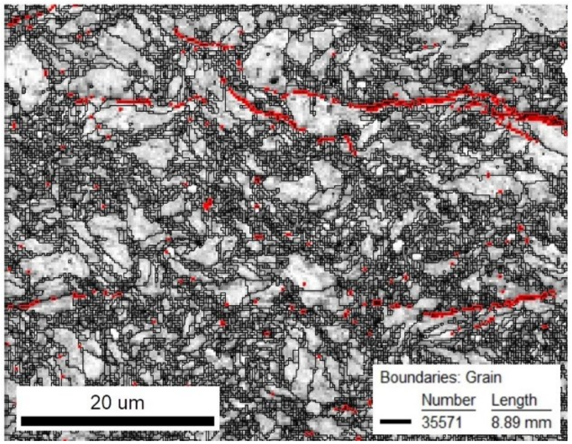


Zircaloy-4 : 1.86 µm (total GB length 8.89 mm)
Zr-Nb alloy : 0.89 µm (total GB length 18.1 mm)

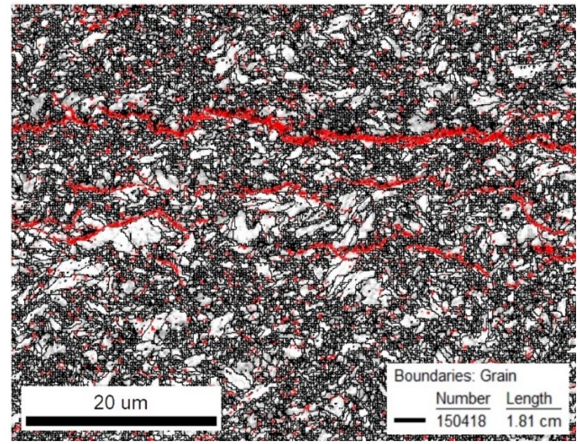
Introduction: Previous Study on the Hydride Embrittlement

- Hydride interconnectivity

Zicaloy-4 (500 wppm)

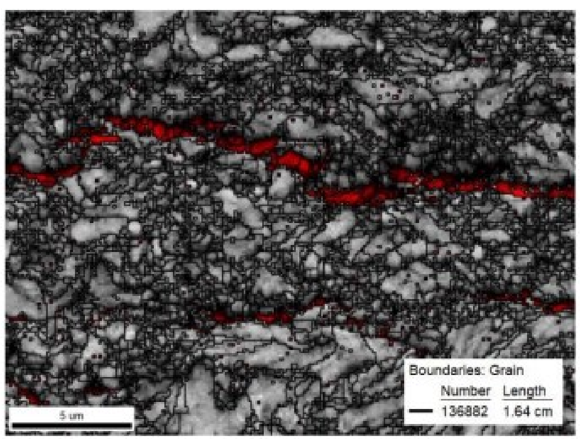


Zr-Nb alloy (500 wppm)

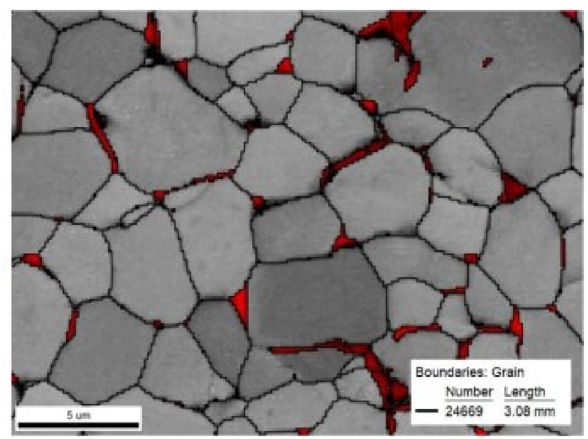


Zr-Nb alloy has better hydride inter-connectivity

- Grain size effect on the GB density and Hydride interconnectivity

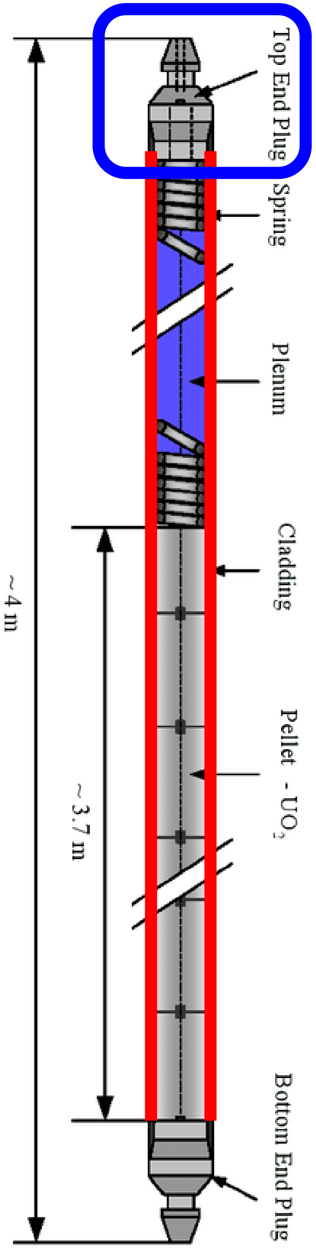


Zr-Nb alloy with no annealing

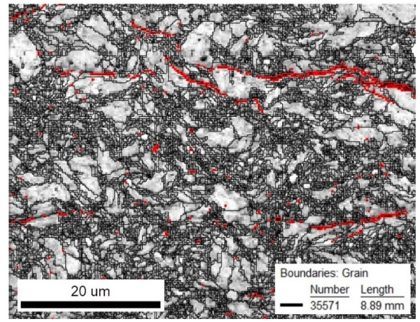


Zr-Nb alloy annealed at 500 ℃ for 3 h

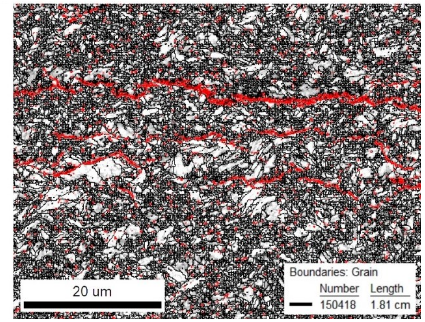
Introduction: Research Motivations



☑ Hydride embrittlement is closely related to the grain size of the cladding material.

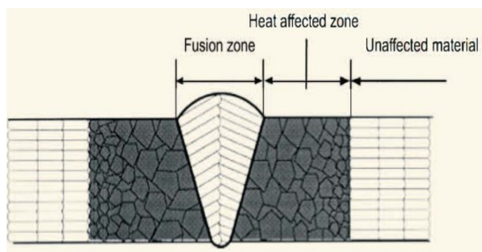


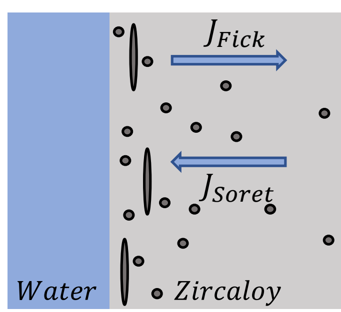
Zircaloy-4 : 1.86 µm

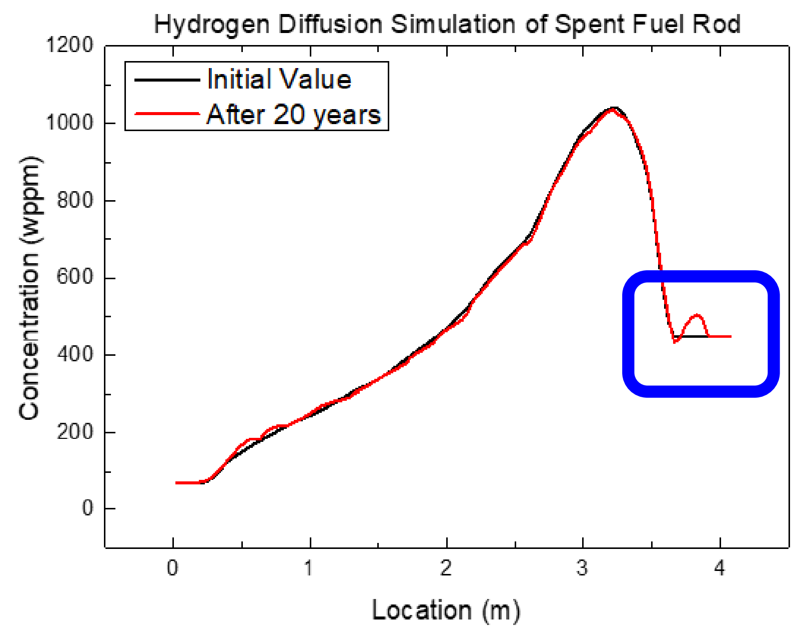


Zr-Nb alloy : 0.89 µm

☑ Hydride embrittlement analysis on the end cap-cladding weld area



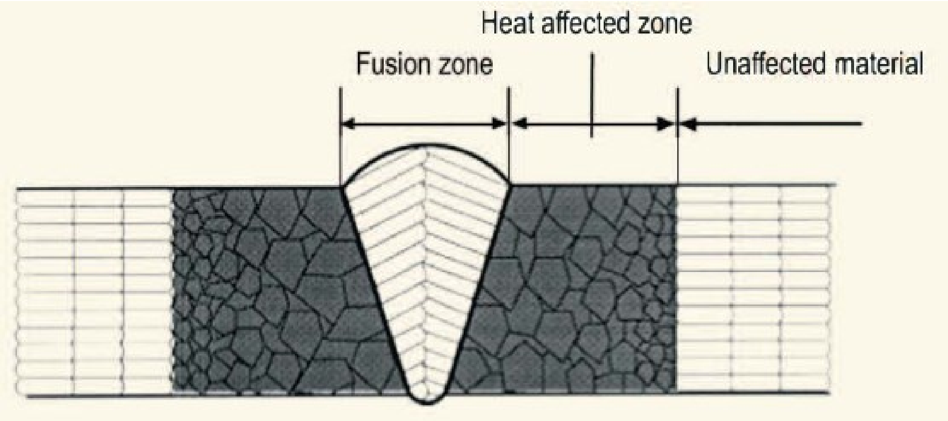


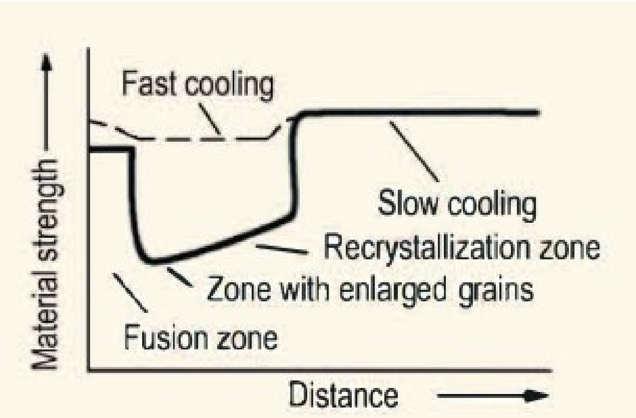


[1] Kammenzind, Bruce F., et al. "Hydrogen pickup and redistribution in alpha-annealed Zircaloy-4." Zirconium in the Nuclear Industry: Eleventh International Symposium. ASTM International, 1996.
[2] Sawatzky, A. "Hydrogen in Zircaloy-2: Its distribution and heat of transport." Journal of Nuclear Materials 2.4 (1960): 321-328.

Introduction: End cap welding zone

- General microstructural features of a weld and the change in material strength [1]

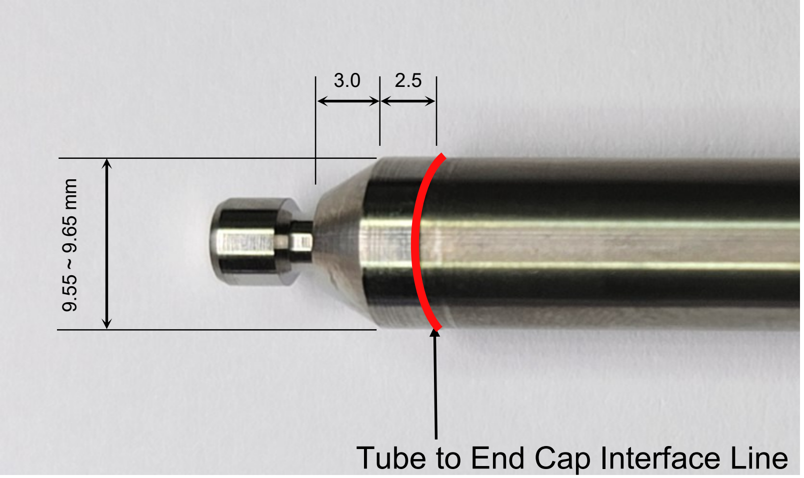




- End Cap welding

  - The welded area of nuclear fuel rods has high possibility of leakage during the operation.

  - To prevent leakage of fissile material during the operation in a nuclear reactor, high integrity of a welding quality is required.



[1] Rudling, Peter, et al. "Welding of Zirconium alloys." IZNA7 special topic report Welding of Zirconium Alloys (2007).

Introduction : Research Goals

☑ Research Goals

1. To investigate the microstructure of the welding area (WZ and HAZ) of Zircaloy.

   * WZ : Welded Zone, HAZ: Heat Affected Zone

2. Hydride embrittlement analysis on the WZ and HAZ of Zr-Nb alloy tube.

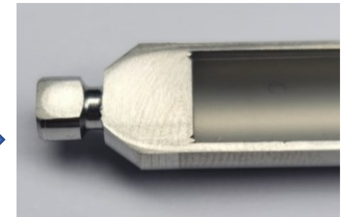
3. To re-examine the welded area structural integrity in terms of SNF management.

Experiment & Discussion: Optical Microscope Analysis

☑ Hydrogen charging and specimen cutting

As received fuel rod

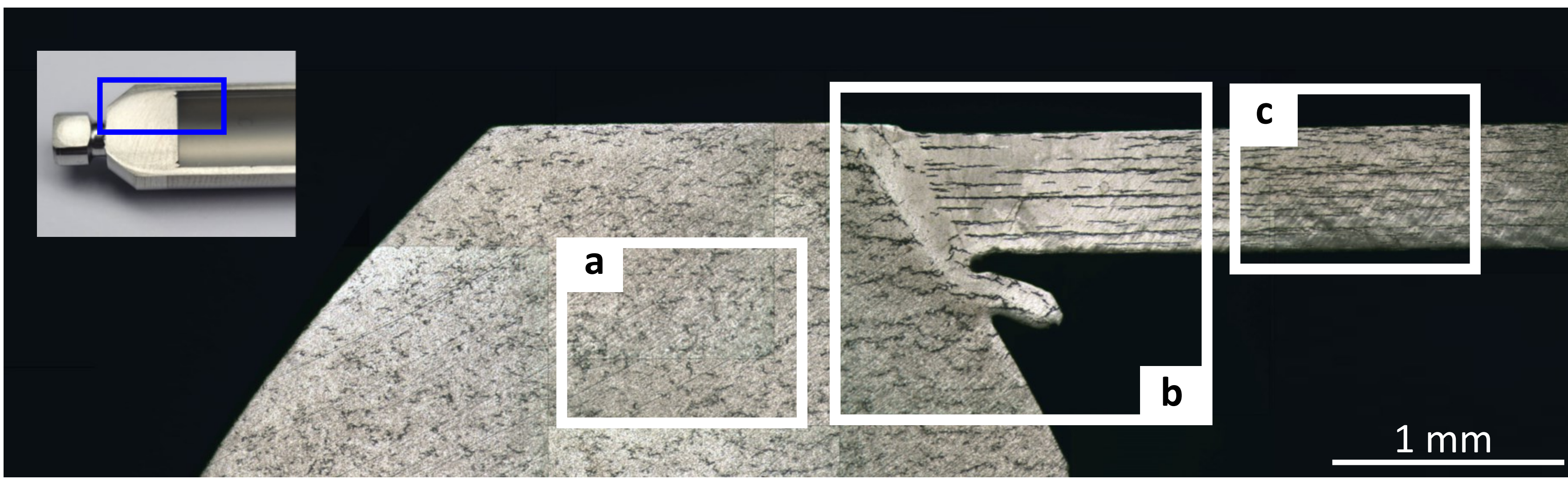
→ Charging H to claddings (400℃ in furnace) →



Half Cutting

→ Analysis (OM)

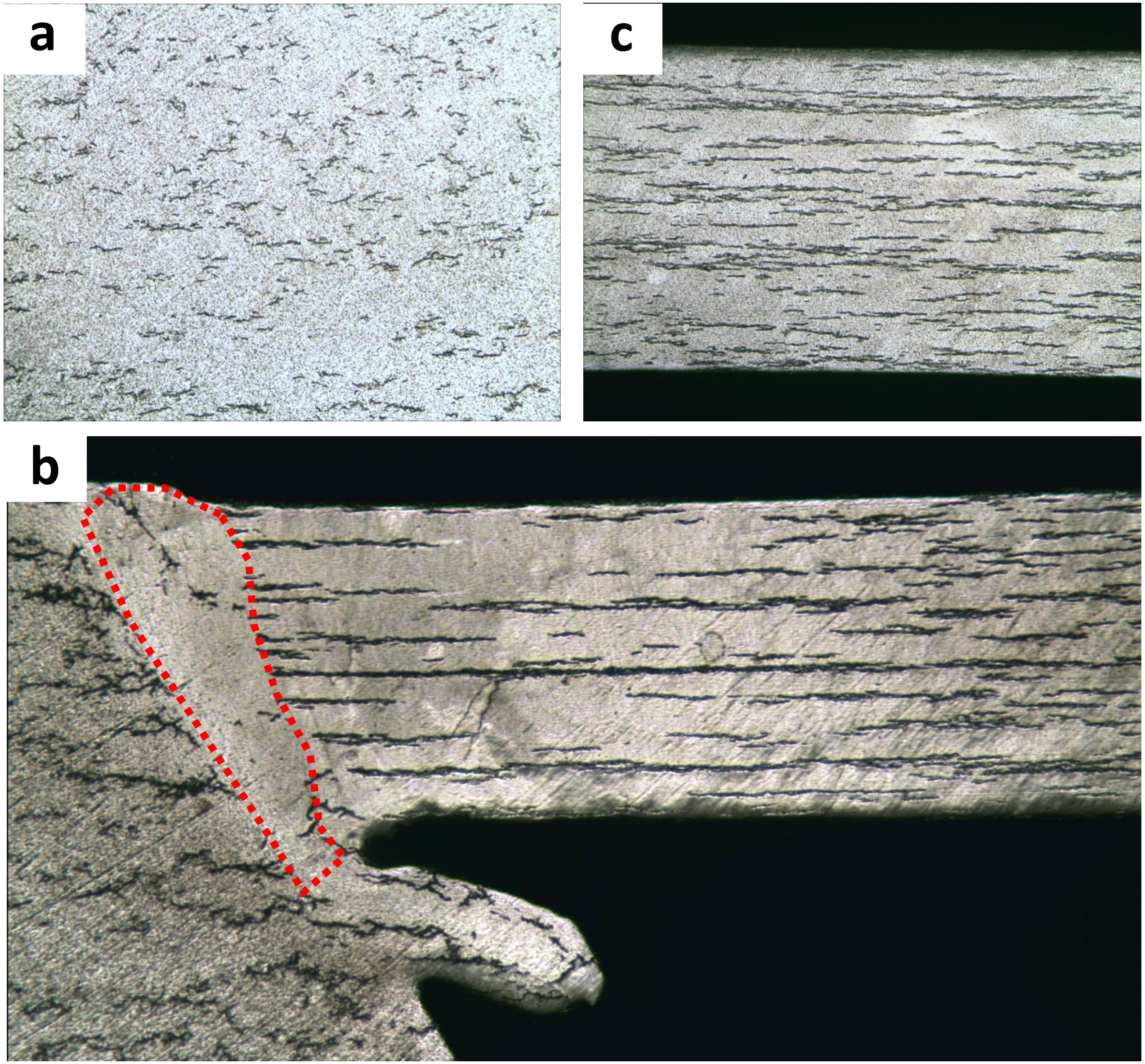
☑ Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)



a: End cap area **b: End cap- cladding welding area** **c: cladding tube area**

Experiment & Discussion: Optical Microscope Analysis

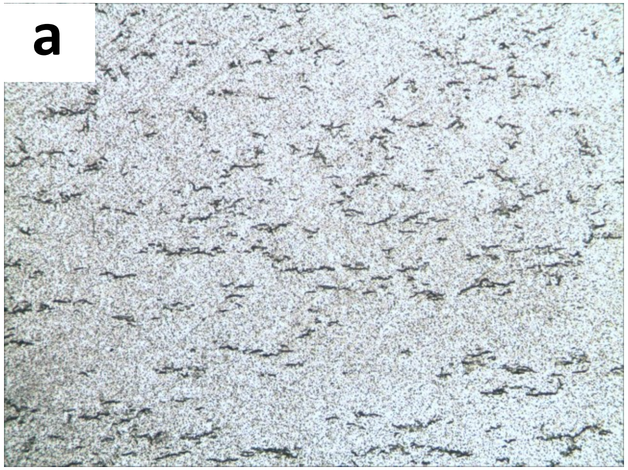
- Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)

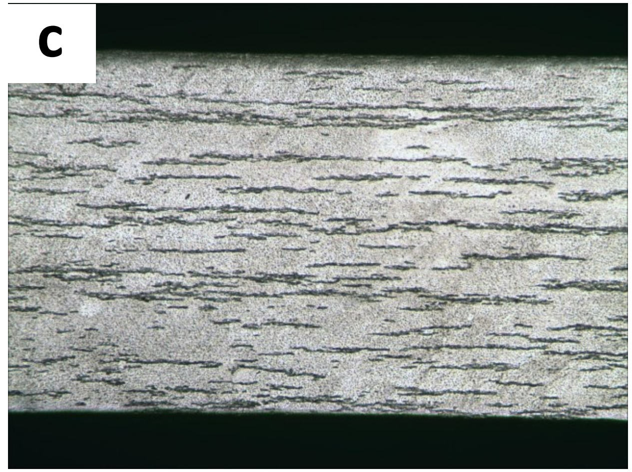


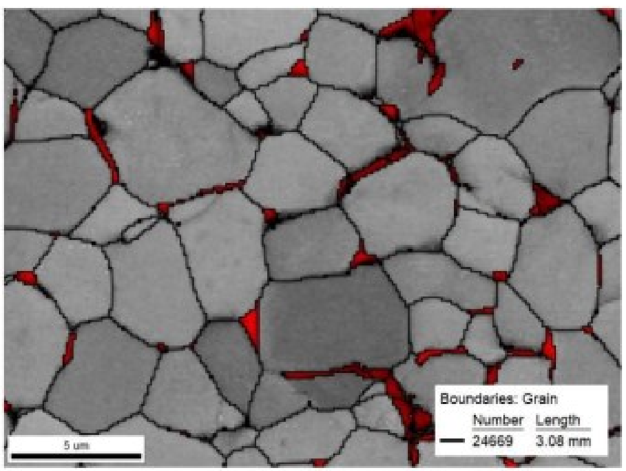
a: End cap area
b: welding area
c: cladding tube area

Experiment & Discussion: Optical Microscope Analysis

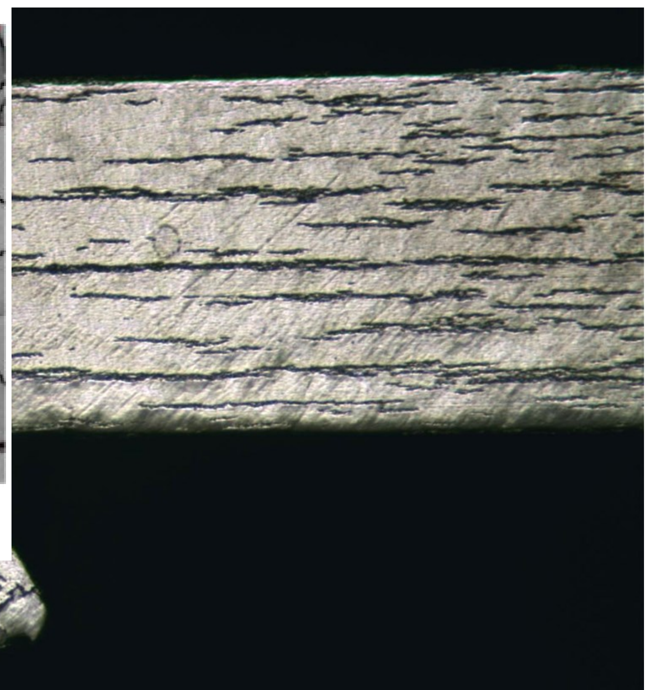
- Morphology of Hydride precipitation (Averaged Hydrogen concentration : 815 wppm)







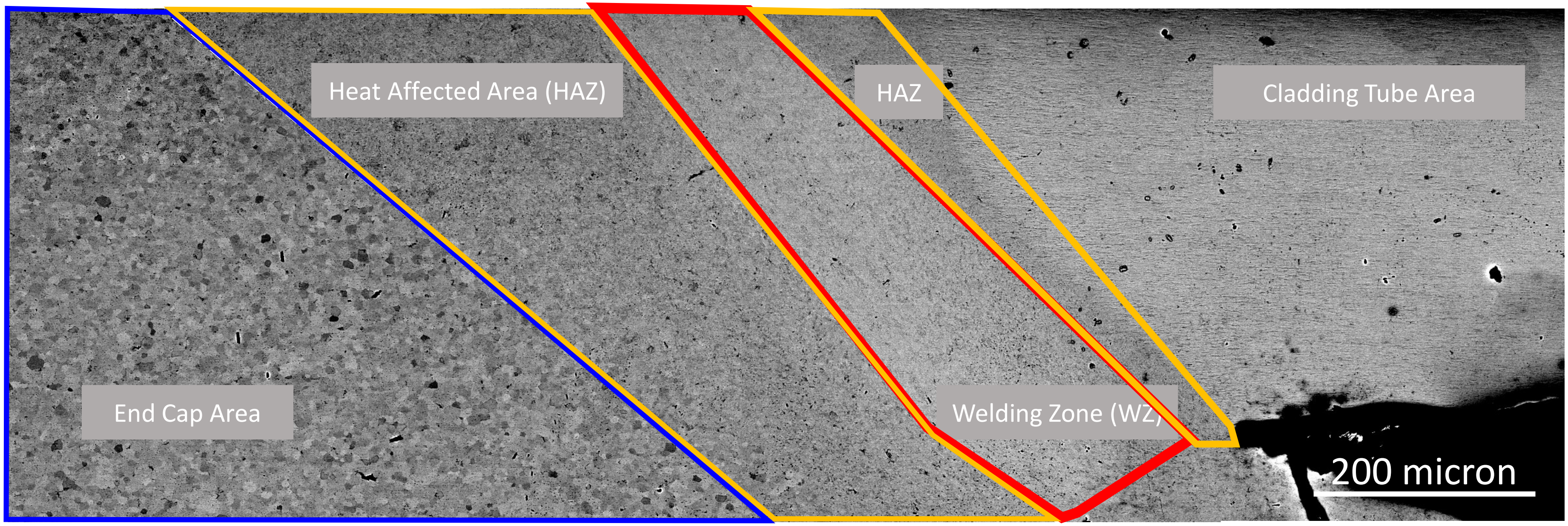
Zr-Nb alloy annealed at 500 ℃ for 3 h



a: End cap area
b: welding area
c: cladding tube area

Experiment & Discussion: BackScattered Electron SEM Analysis

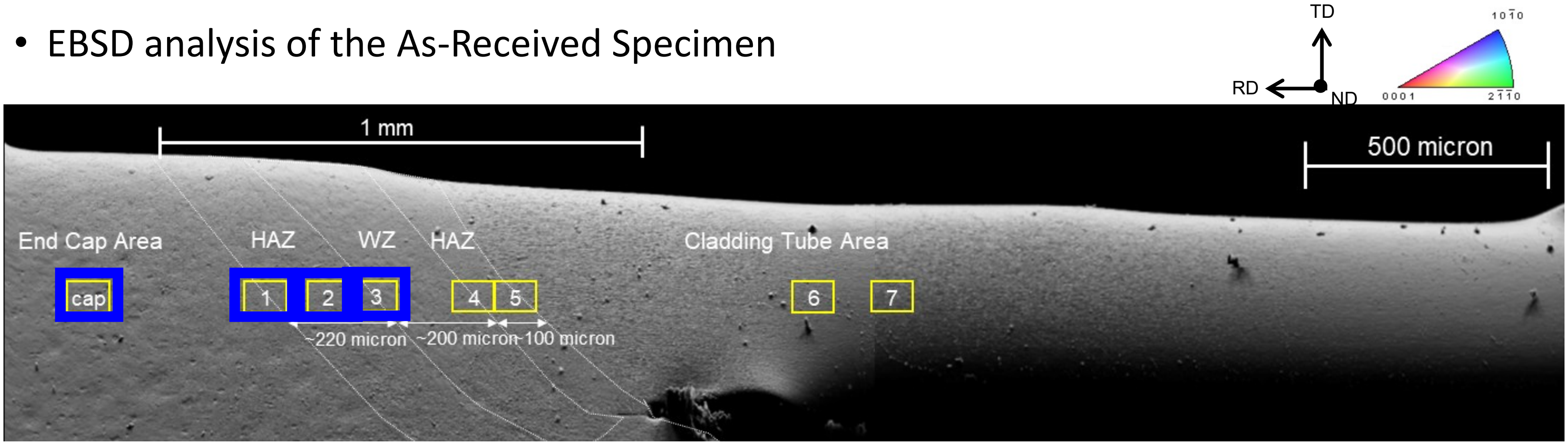
- BSE SEM analysis

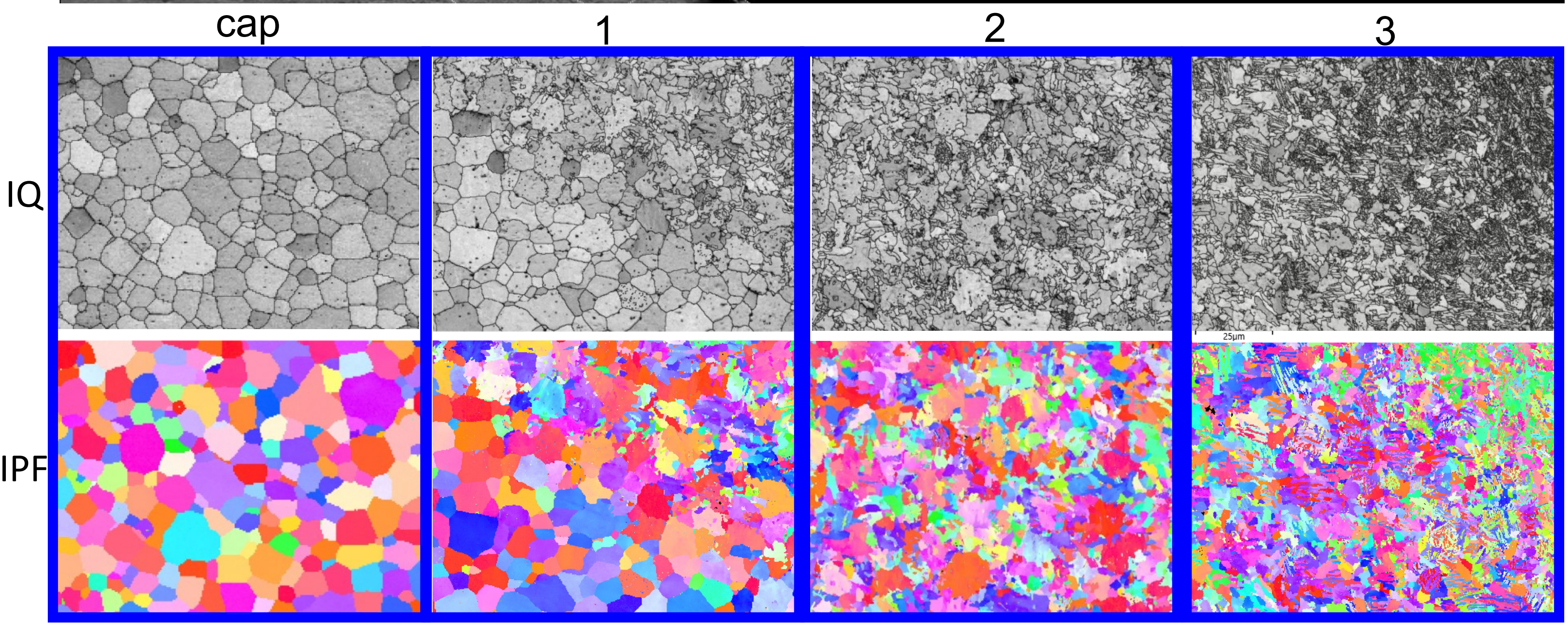


Through BSE SEM Macrographs of welded area,
end cap area, HAZ, WZ, and tube area are roughly distinguishable.

Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen





Experiment & Discussion: EBSD analysis

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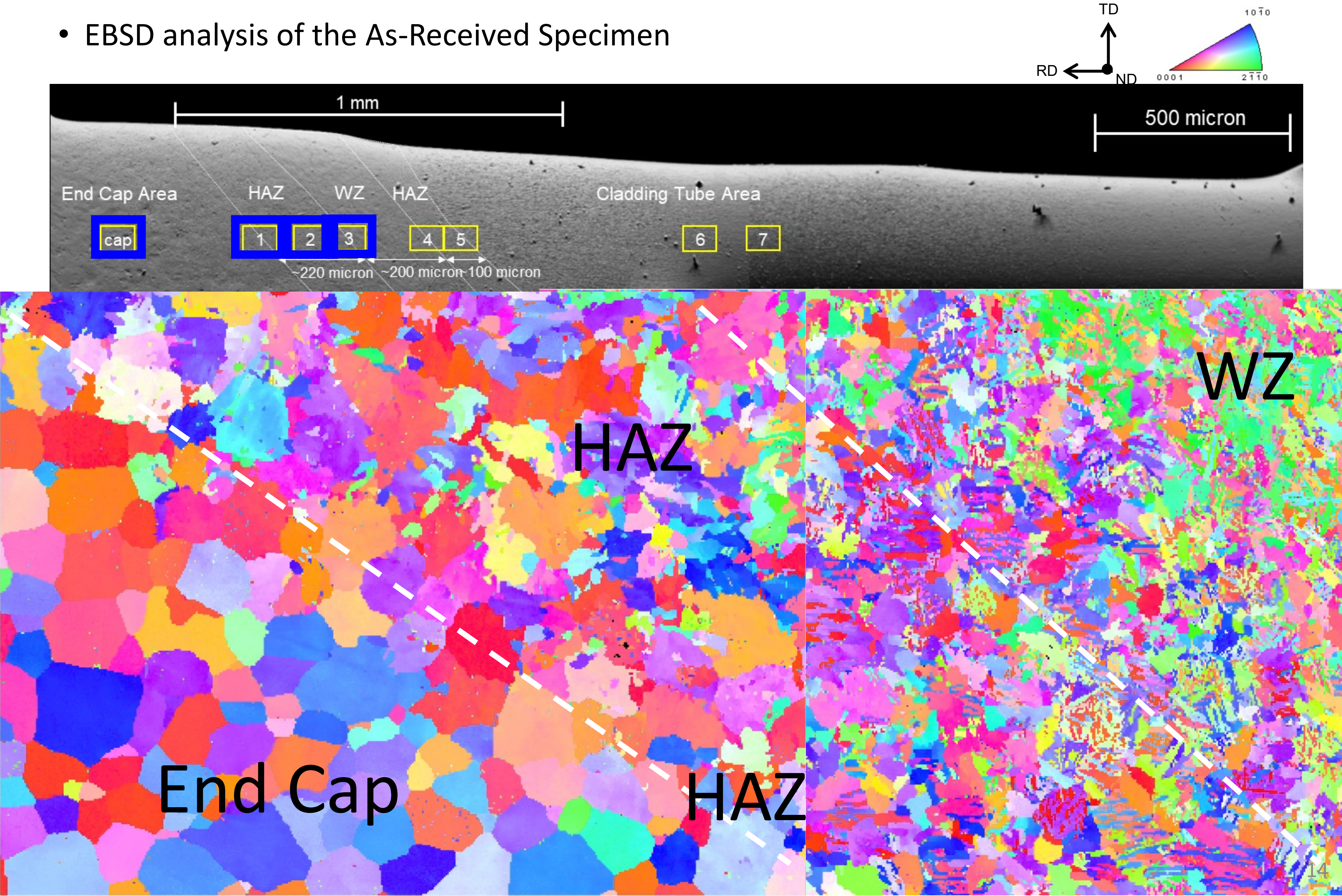

Experiment & Discussion: EBSD analysis

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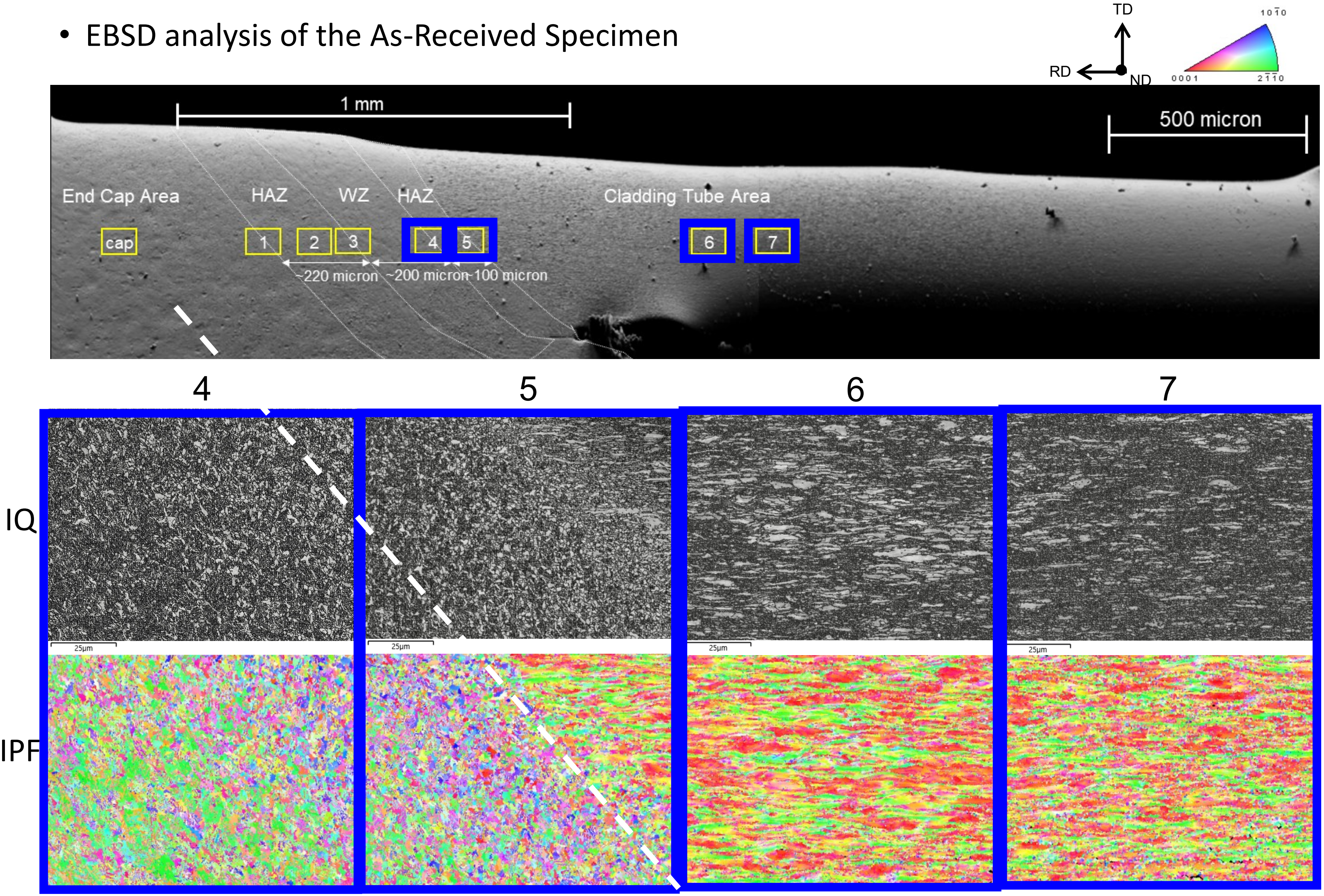
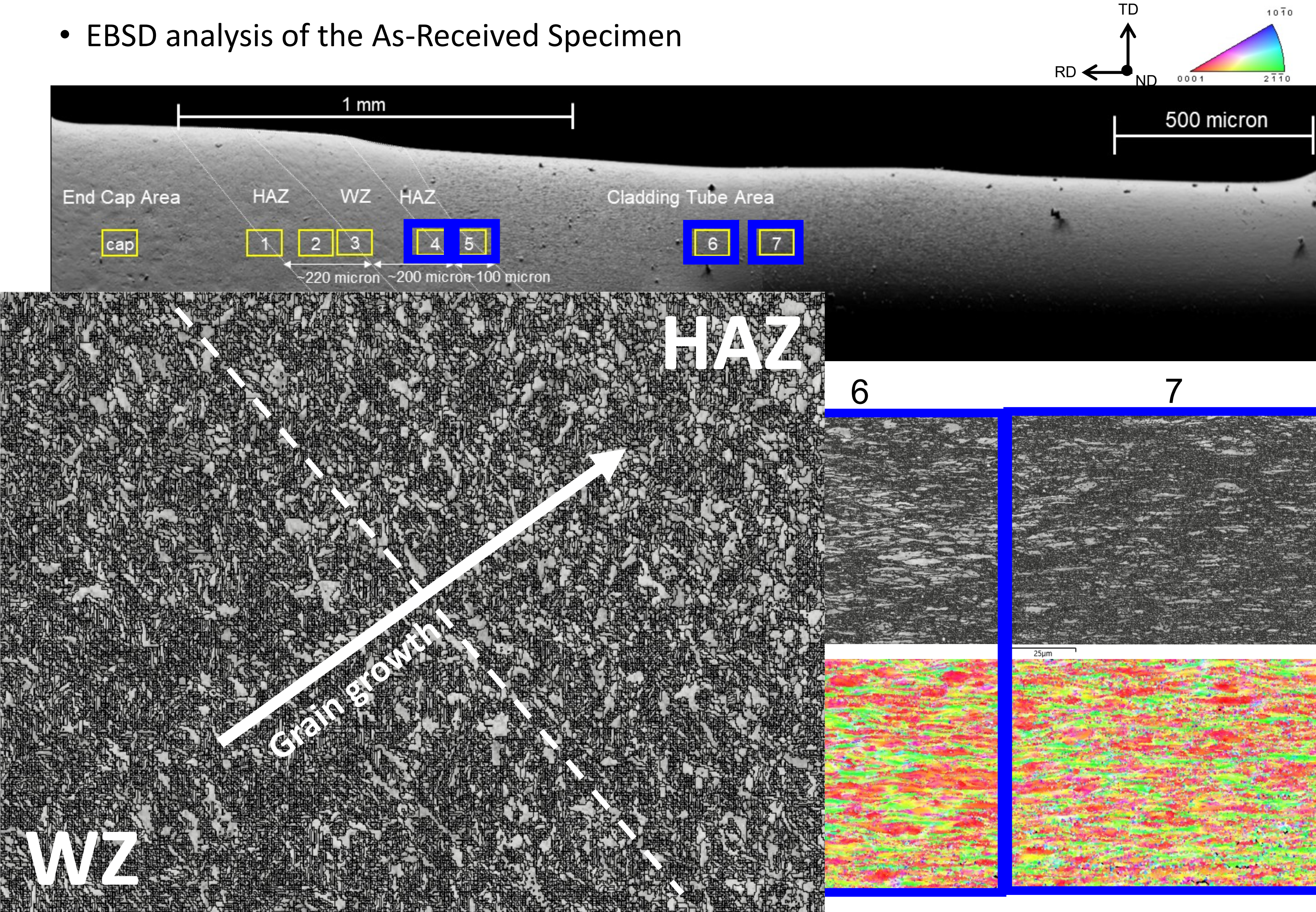


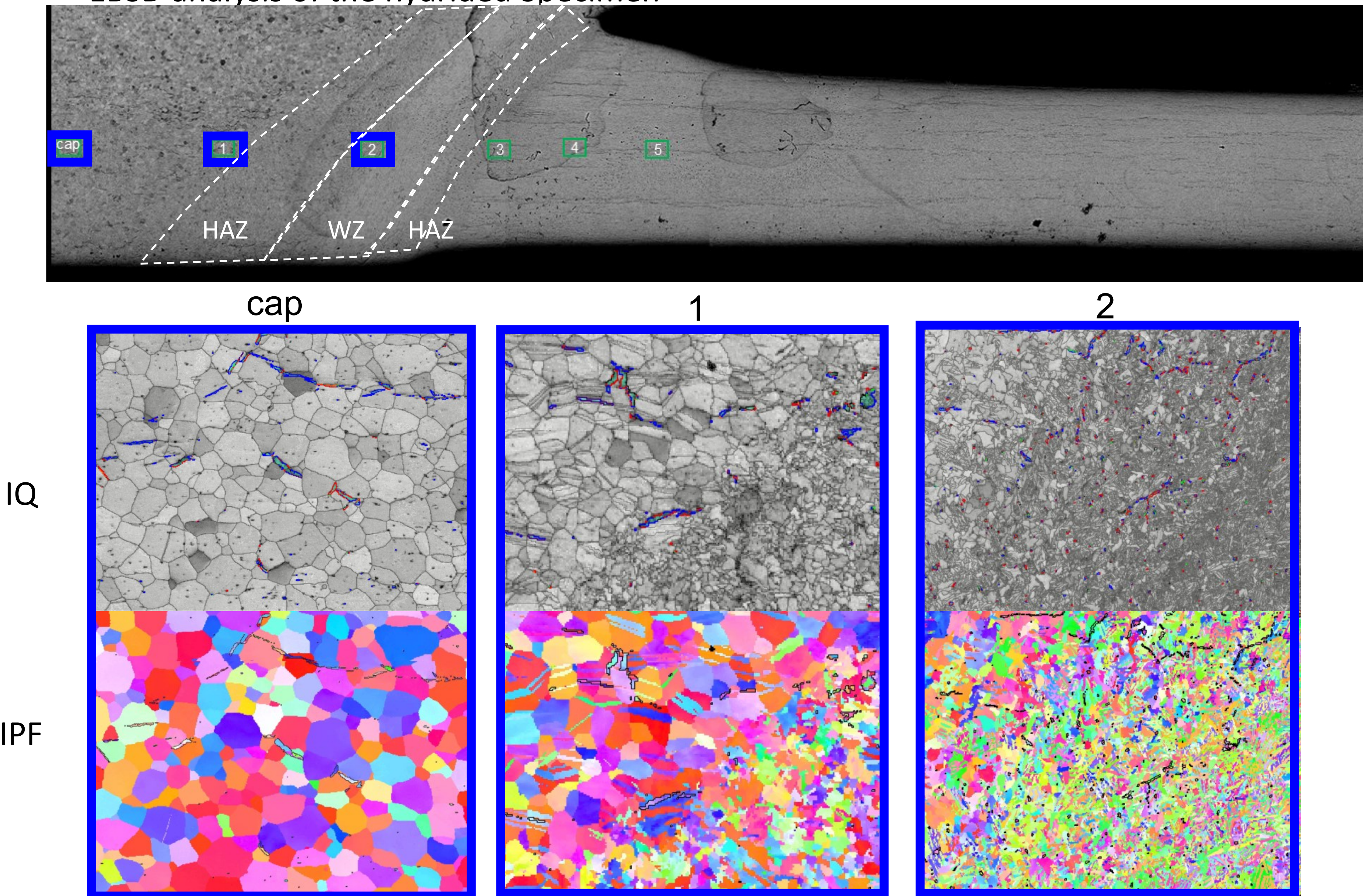
Experiment & Discussion: EBSD analysis

- EBSD analysis of the As-Received Specimen



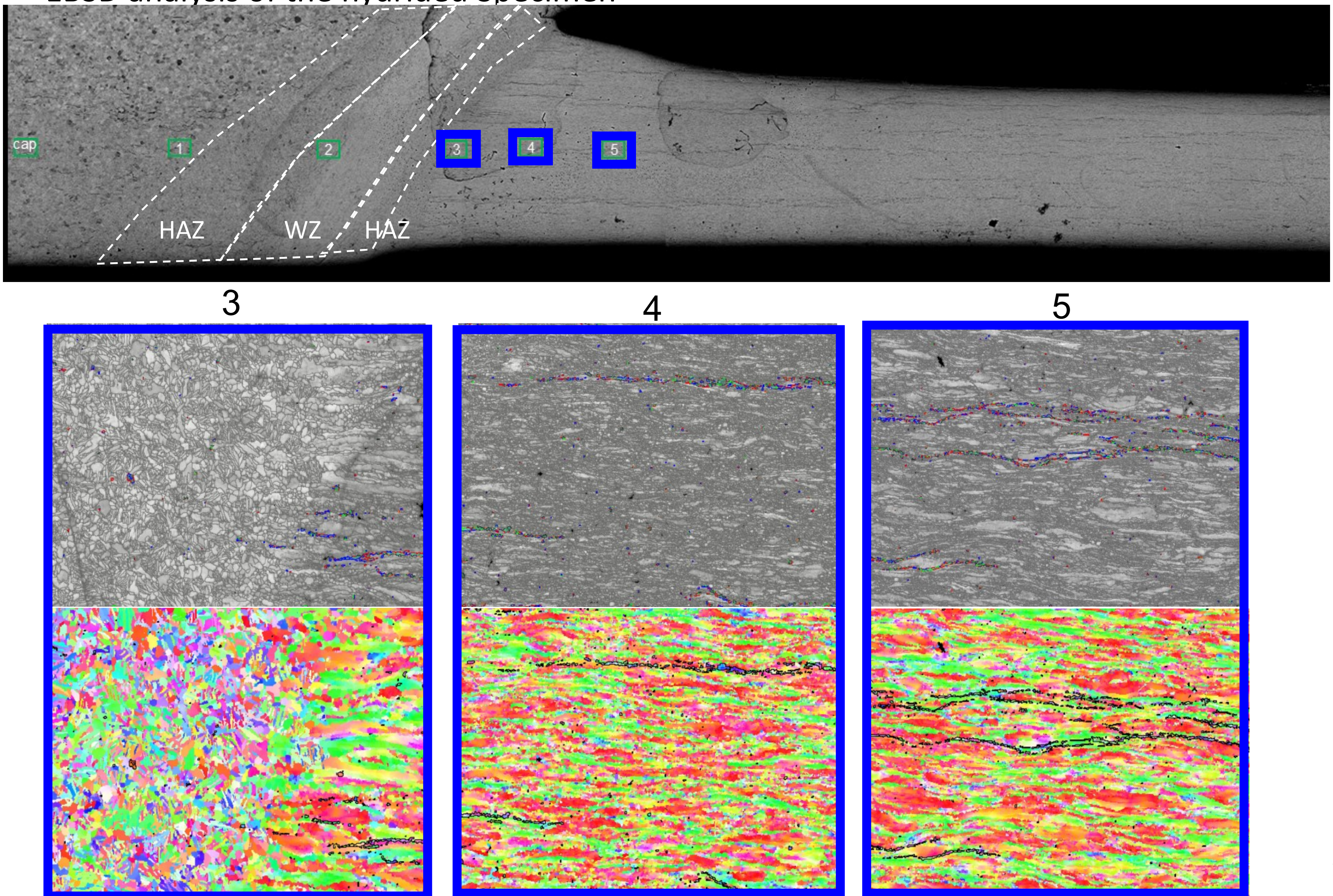
Experiment & Discussion: EBSD analysis

- EBSD analysis of the hydrided Specimen



Experiment & Discussion: EBSD analysis

- EBSD analysis of the hydrided Specimen

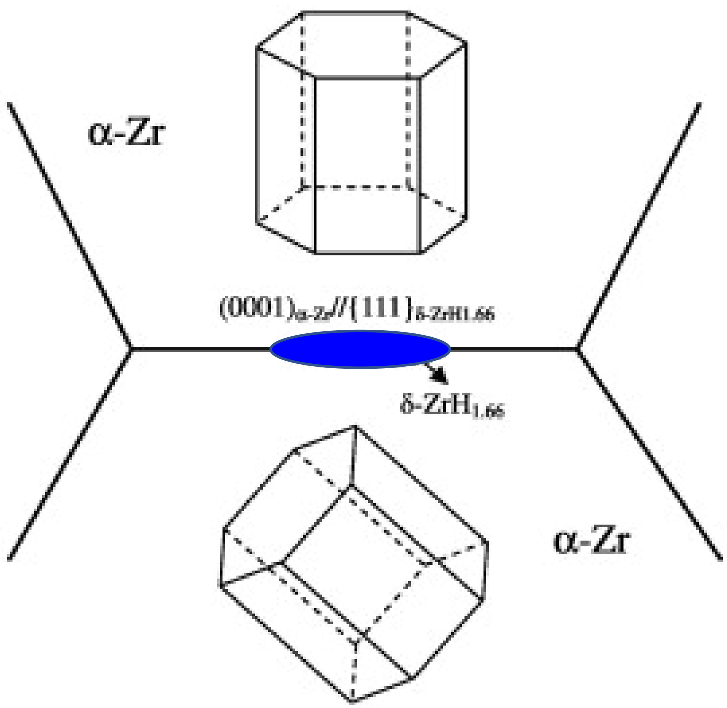


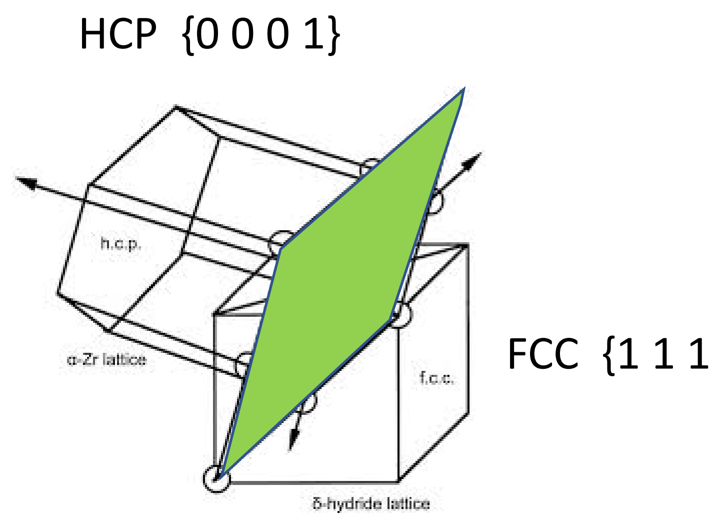
Experiment & Discussion: EBSD analysis

- Zr-Hydride interface orientation analysis: Misfit strain (χ) calculation

$$\Delta G_{strain} = \frac{6\,\mu\,\eta\,\gamma}{\eta(\gamma-1)+1}$$

$$\Delta G = -V\Delta G_{chem} + A\Delta G_{surface} + V \quad - S\Delta G_{GB}$$



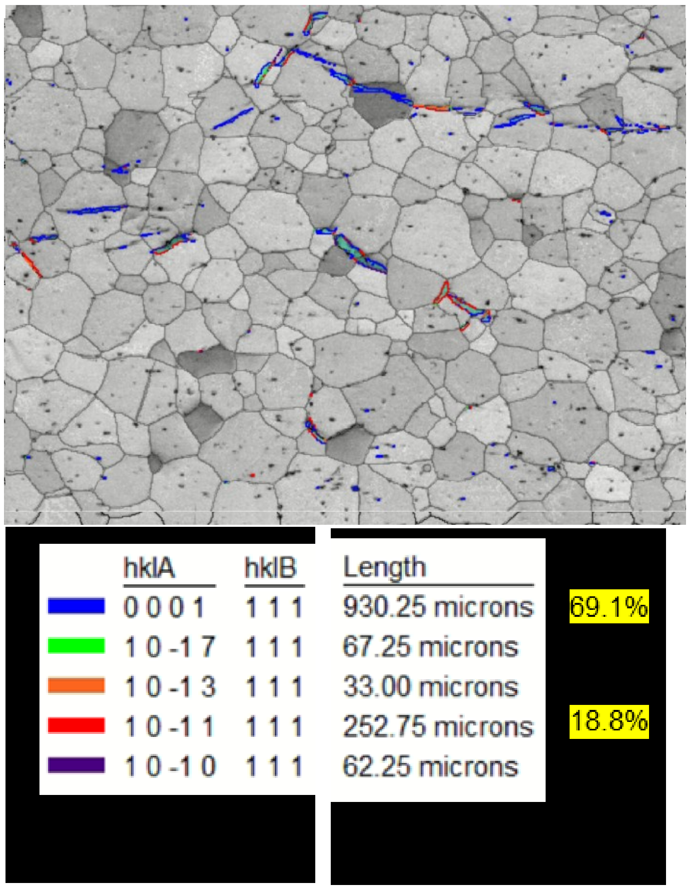


[1] Qin, W., et al. "Intergranular δ-hydride nucleation and orientation in zirconium alloys." Acta Materialia 59.18 (2011): 7010-7021.

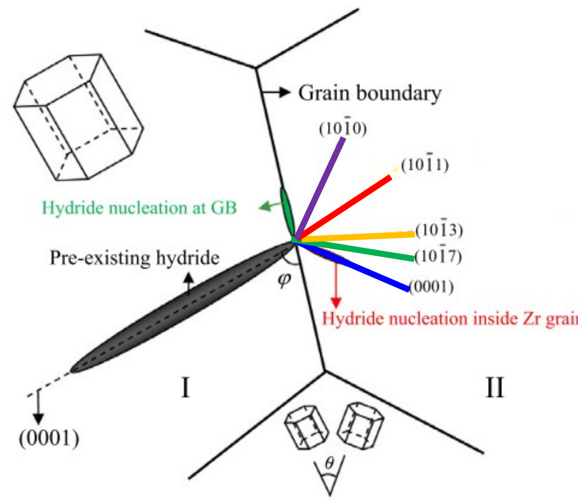
Experiment & Discussion: EBSD analysis

- Zr-Hydride interface orientation analysis: Misfit strain (χ) calculation

cap



Averaged Misfit strain ($\bar{\chi}$) = **0.059531**

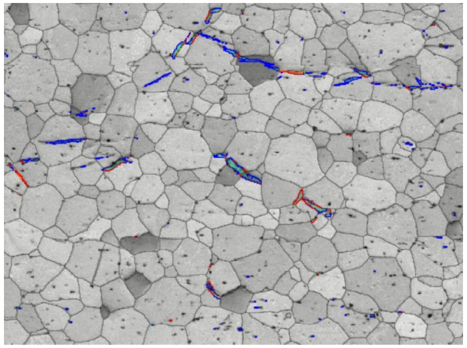


Crystallographic Orientation Relationship	Misfit strain (χ)
$\{0\,0\,0\,1\}_\alpha//\{1\,1\,1\}_\delta$	0.0545
$\{1\,0\,\bar{1}\,7\}_\alpha//\{1\,1\,1\}_\delta$	0.0561
$\{1\,0\,\bar{1}\,3\}_\alpha//\{1\,1\,1\}_\delta$	0.0614
$\{1\,0\,\bar{1}\,1\}_\alpha//\{1\,1\,1\}_\delta$	0.0738
$\{1\,0\,\bar{1}\,0\}_\alpha//\{1\,1\,1\}_\delta$	0.0795

[1] Qin, W., et al. "Intergranular δ-hydride nucleation and orientation in zirconium alloys." Acta Materialia 59.18 (2011): 7010-7021.

Experiment & Discussion: EBSD analysis

cap

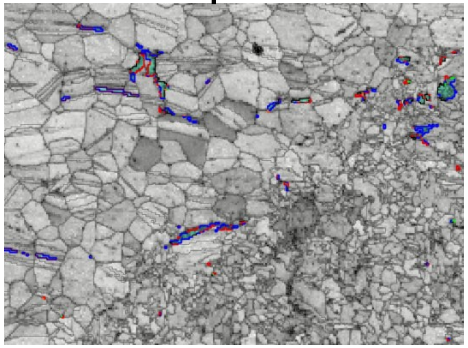


$\bar{\chi}$

hklA	hklB	Length	
0 0 0 1	1 1 1	930.25 microns	69.1%
1 0 -1 7	1 1 1	67.25 microns	
1 0 -1 3	1 1 1	33.00 microns	
1 0 -1 1	1 1 1	252.75 microns	18.8%
1 0 -1 0	1 1 1	62.25 microns	

0.0595

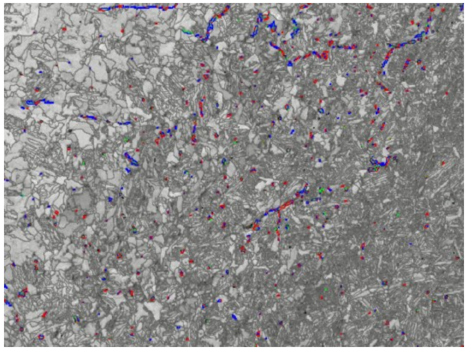
1: Cap - HAZ



hklA	hklB	Length	
0 0 0 1	1 1 1	353.50 microns	46.9%
1 0 -1 7	1 1 1	101.50 microns	
1 0 -1 3	1 1 1	12.00 microns	
1 0 -1 1	1 1 1	158.50 microns	21.0%
1 0 -1 0	1 1 1	127.50 microns	16.9%

0.0631

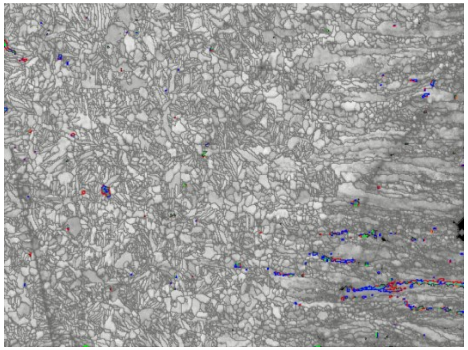
2: HAZ-WZ



hklA	hklB	Length	
0 0 0 1	1 1 1	433.75 microns	46.3%
1 0 -1 7	1 1 1	95.75 microns	
1 0 -1 3	1 1 1	12.50 microns	
1 0 -1 1	1 1 1	355.25 microns	37.9%
1 0 -1 0	1 1 1	40.50 microns	

0.0631

3: WZ-HAZ

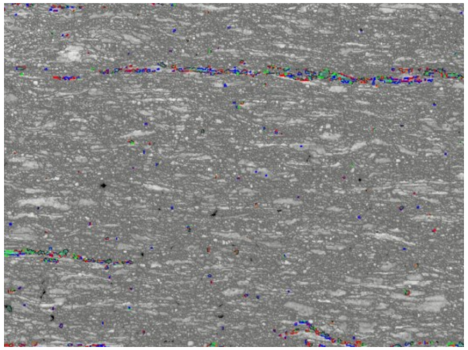


$\bar{\chi}$

hklA	hklB	Length	
0 0 0 1	1 1 1	84.63 microns	51.7%
1 0 -1 7	1 1 1	15.25 microns	
1 0 -1 3	1 1 1	10.63 microns	
1 0 -1 1	1 1 1	42.75 microns	26.1%
1 0 -1 0	1 1 1	10.50 microns	

0.0617

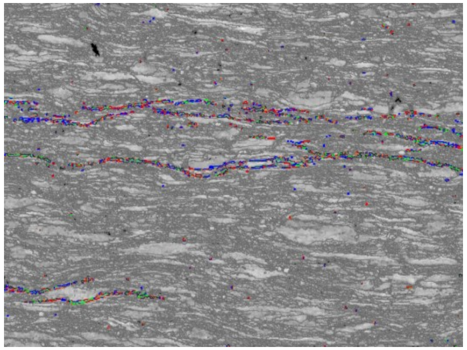
4: Tube



hklA	hklB	Length	
0 0 0 1	1 1 1	191.00 microns	36.2%
1 0 -1 7	1 1 1	89.50 microns	17.0%
1 0 -1 3	1 1 1	46.25 microns	
1 0 -1 1	1 1 1	150.75 microns	28.6%
1 0 -1 0	1 1 1	50.00 microns	

0.0633

5 : Tube



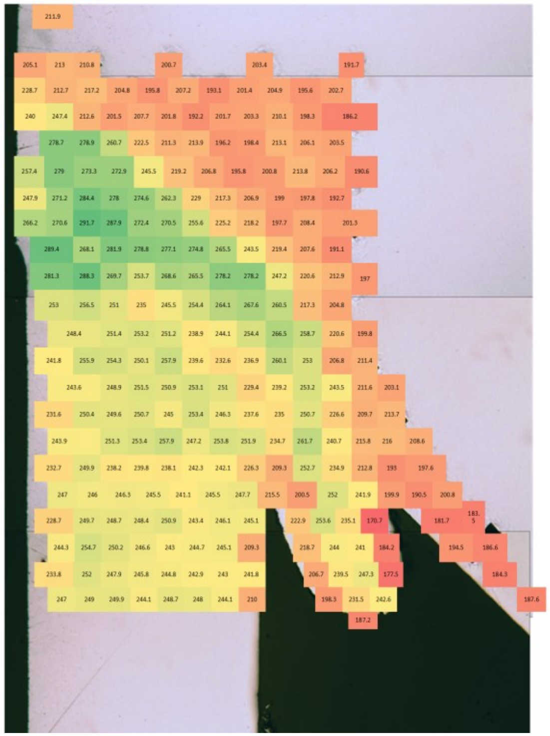
hklA	hklB	Length	
0 0 0 1	1 1 1	313.00 microns	36.7%
1 0 -1 7	1 1 1	146.50 microns	17.2%
1 0 -1 3	1 1 1	74.75 microns	
1 0 -1 1	1 1 1	248.00 microns	29.1%
1 0 -1 0	1 1 1	71.25 microns	

0.0630

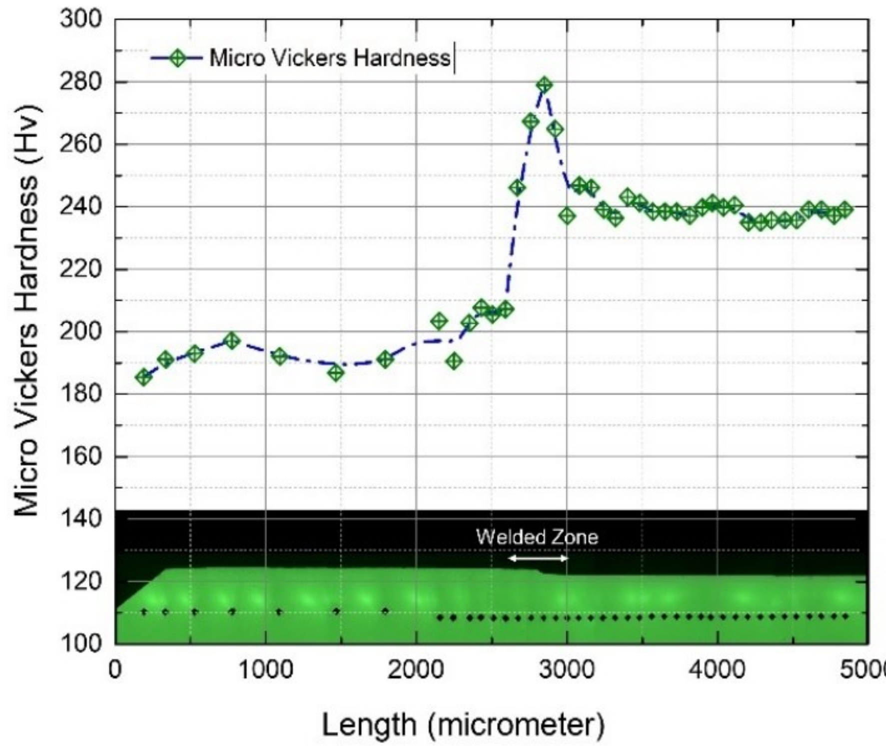
$\bar{\chi} \approx 0.0595 \sim 0.0633$

Experiment & Discussion: Hardness test (Vickers)

- Micro Vickers Hardness Result of As-Received Specimen



▲ Hardness mapping



▲ Hardness mapping (linear)

Vickers Hardness test with 0.3kgf, 15 seconds
Hardness value is the highest at the Welding Zone.

Experiment & Discussion: Thermodynamic model

- Hardness-Shear modulus relations

Hardness (Hv) → Hardness -Yield strength (σ_y) → Yield strength-Elastic modulus → Elastic modulus(E) -Shear modulus(G)

$$H_V \approx 3 \cdot \sigma_y$$

$$H = \frac{2\sigma_y}{3}\left\{1 + \ln\left[\frac{E}{3(1-\nu)\sigma_y}\right]\right\}$$

$$E = 2G(1+\nu) = 3K(1-2\nu).$$

<Shear modulus, G>

End cap : 30.1 GPa / Welding Zone : 42.7 Gpa / Tube : 36.4 GPa

- Hydride nucleation Gibbs free energy equation [1]

$$\Delta G = -V\Delta G_{chem} + A\Delta G_{surface} + V \quad - S\Delta G_{GB}$$

$$= \frac{6 \quad \eta\gamma\chi^2}{\eta(\gamma-1)+1}$$

Strain energy per unit volume of δ-hydride formation

ΔG_{chem}	Chemical free energy per unit volume
$\Delta G_{surface}$	the interphase energy btw nucleus and matrix
ΔG_{GB}	the GB energy between the parent grains
χ	misfit strain
η	$\eta = (1 + \nu)/3(1 - \nu)$
γ	the ratio of the bulk modulus of the precipitate to that of the matrix

[1] Qin, W., et al. "Intergranular δ-hydride nucleation and orientation in zirconium alloys." Acta Materialia 59.18 (2011): 7010-7021.

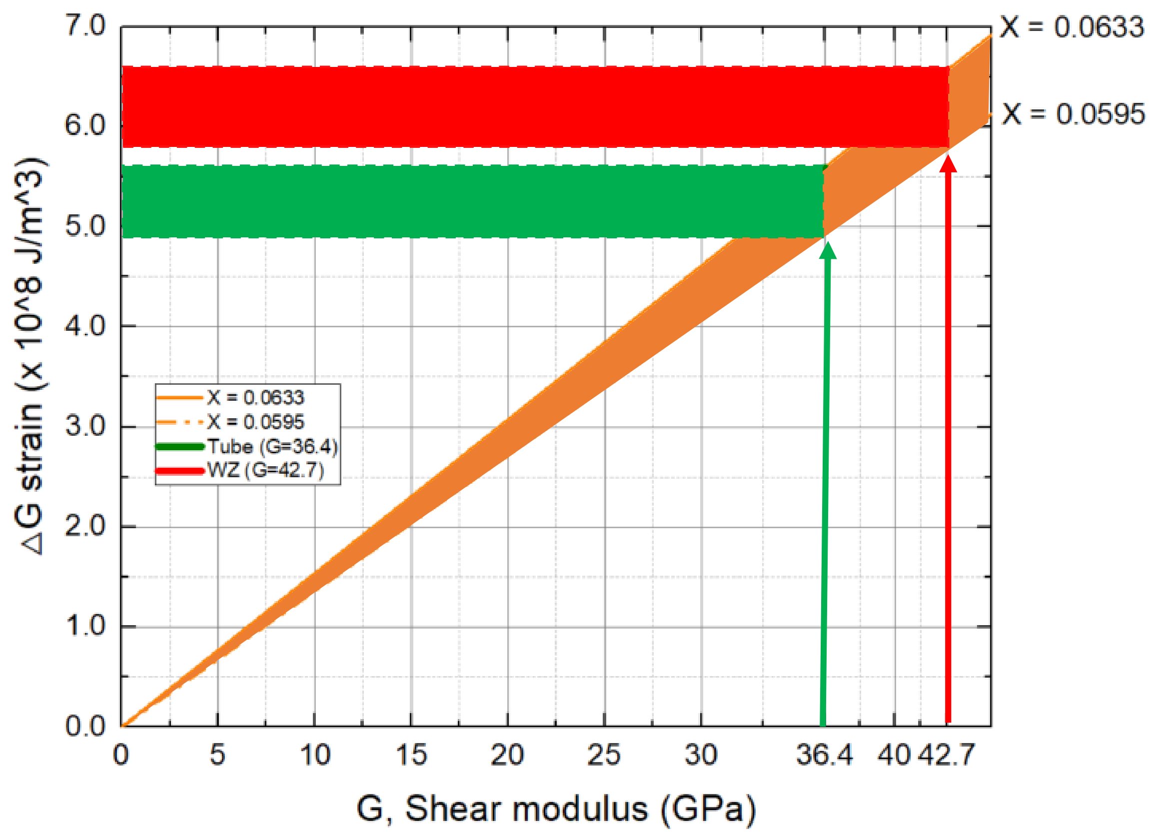
Experiment & Discussion: Thermodynamic model

- Shear modulus- △G strain curve

χ misfit strain

WZ (G=42.7 GPa)
△G strain : 5.81 ~ 6.56 [x 10^8 J/m^3]

Cladding tube (G=36.4 GPa)
△G strain : 4.95 ~ 5.59 [x 10^8 J/m^3]



$$\Delta G_{strain} = \frac{6\mu\eta\gamma\chi^2}{\eta(\gamma-1)+1}$$

WZ (G=42.7 GPa) ＞ Cladding tube (G=36.4 GPa)

- Hydride precipitation at the WZ is more difficult than at the cladding tube.

Conclusion and Path forward

1. In the end cap to tube welding, WZ and HAZ are within the 1 mm length area.

2. Microstructure mapping via EBSD on the end cap to cladding welding area is completed.

3. WZ and HAZ seems to have hydride embrittlement resistance.

   - Hardness of WZ is the highest among other area in the fuel rod.
   - Martensite phase in the WZ and HAZ, increases the stiffness of the material
   - shear modulus increase in the WZ and HAZ
   - G strain energy of WZ is much higher than cladding tube (using thermodynamic model)

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