ATF開発に向けた基礎研究とその展開

Development of Metal-Coated Zircaloy for Accident-Tolerant Fuels

Hiroaki ABE
The University of Tokyo

Collaborators:
The Univ Tokyo: K. Takanabe, A. Nakayama, S. Kano, H.L. Yang (Shanghai Jiaotong University), L.J. Cui (Chengdu Univ.), K.J. Wei, B.Li, N. Nikolova, Z.Q. Wei, J.A. Jovellana
Tohoku Univ: Y. Chen, T. Davey
JAEA: M. Yamaguchi
MHI (NDC): K. Ogata, Y. Shinohara

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Contents

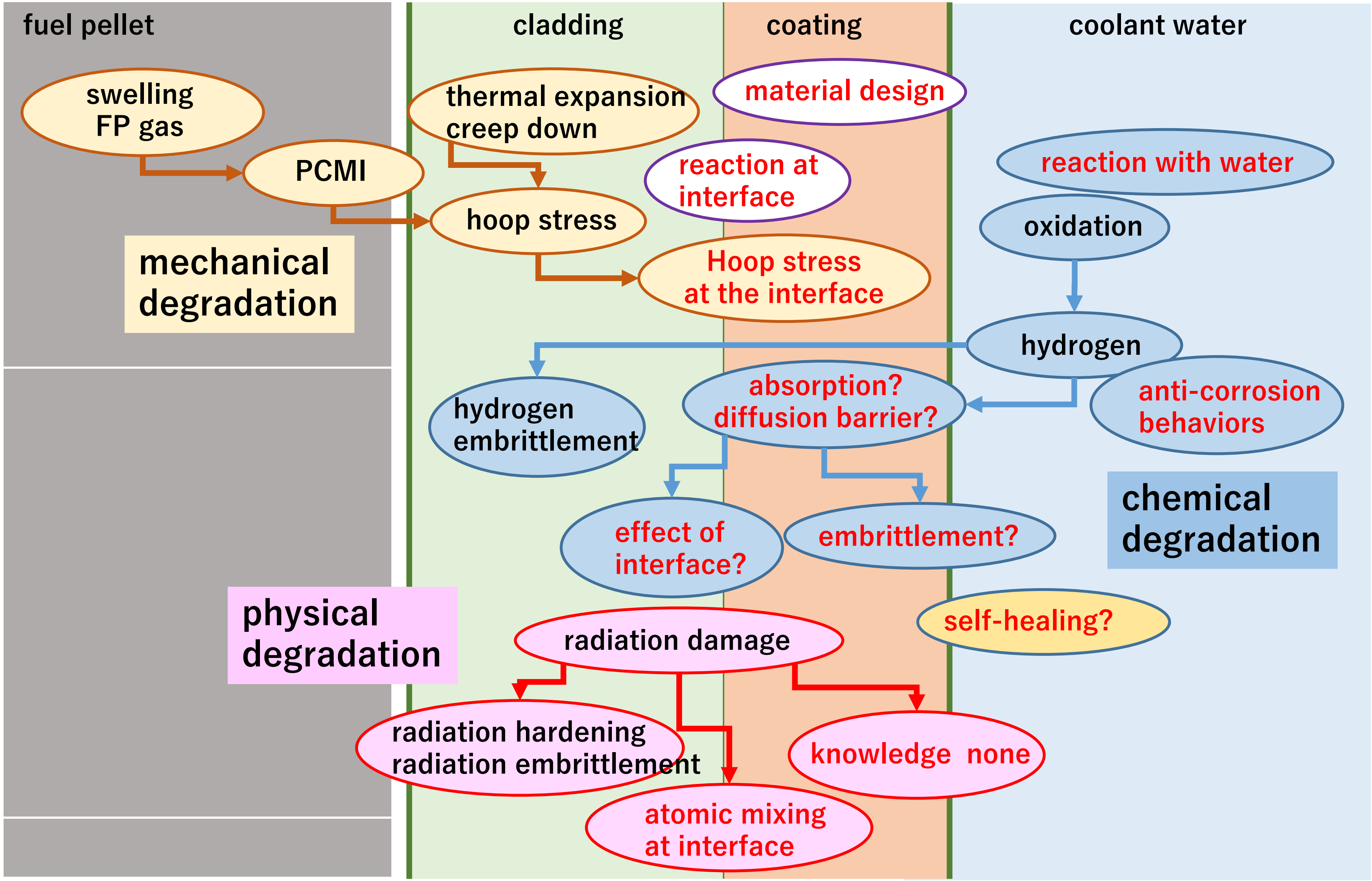
Accident Tolerant Fuels（ATFs）

OECD/NEA and AESJ

	integrity	tech level	terms
・modified zircaloy	mid	high	short
・Cr-coated Zr-alloy	mid	low～high	short
・Zr-coated Mo-alloy	?	low	mid～long ?
・FeAlCr、ODS	high	low～mid	mid
・SiC composite	very high	low	very long

The Cr-coated Zr alloy incorporates the idea of suppressing reactions with other parts at high temperature. Since Zr alloys are practical materials for industrial use, it is expected as the highest possible and near-term introduction in commercial nuclear plants.

Cr被覆ジルコニウム合金の課題



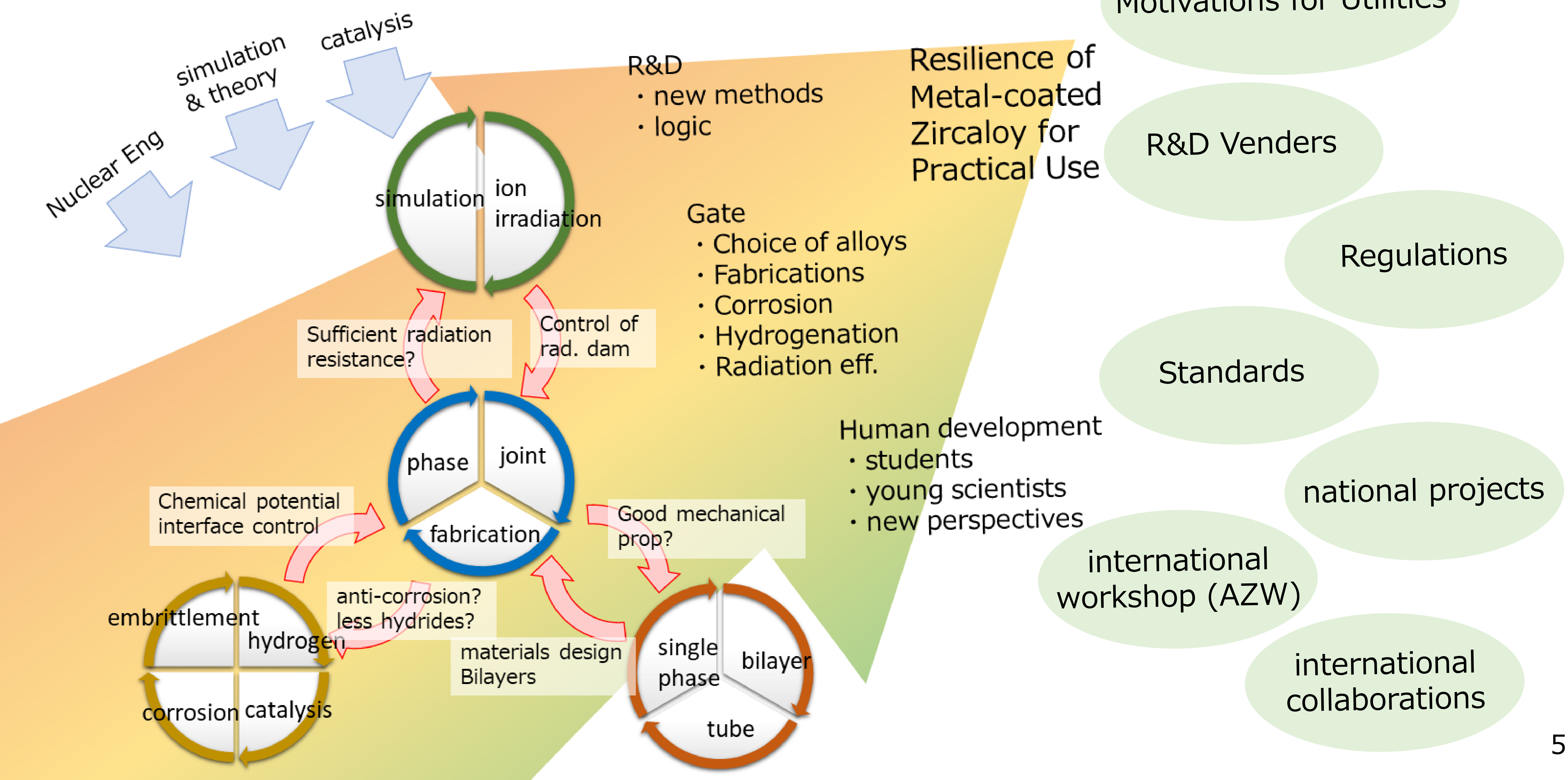
Issues

Coating
- **materials design**
- **radiation effects**

Surface oxide
- **reaction**
- **reaction with H_2**

Coating/zircaloy interface
- **stability at HT**
- **radiation effects**
- **reaction with H_2**

structure of this project and roadmap



Contents

合金設計 (DFT)

Cr-X alloy as a coating material for ATF

Basic idea on searching elements by DFT calculations

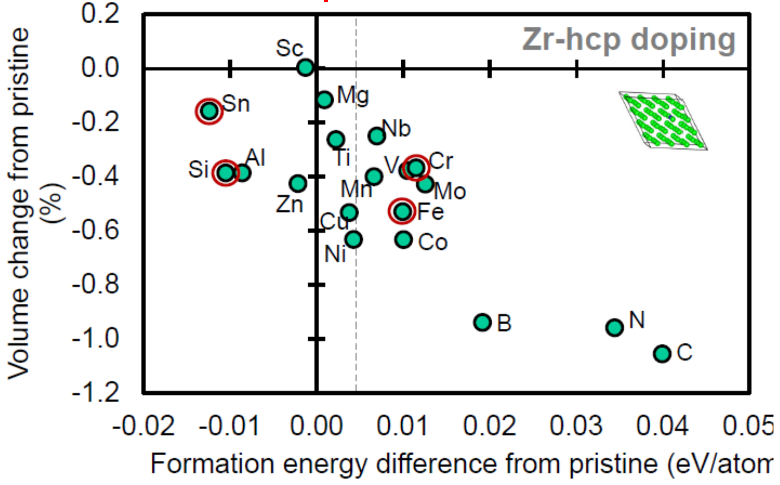
- X in bcc-Cr stable as solid solution (ΔE_f: small)
- X in hcp-Zr stable as solid solution (ΔE_f: small)
- X in $ZrCr_2$ destabilizes the Laves phase (ΔE_f : large)
- Small volume change due to doping to avoid strain and cracking
- Low neutron absorption cross section: requirement for nuclear

Cr-X

Sn, Zn, Mg
$\Delta E_f(C15) < \Delta E_f(Cr)$,
most likely migrate to Laves phase,
act as suppressing elements.

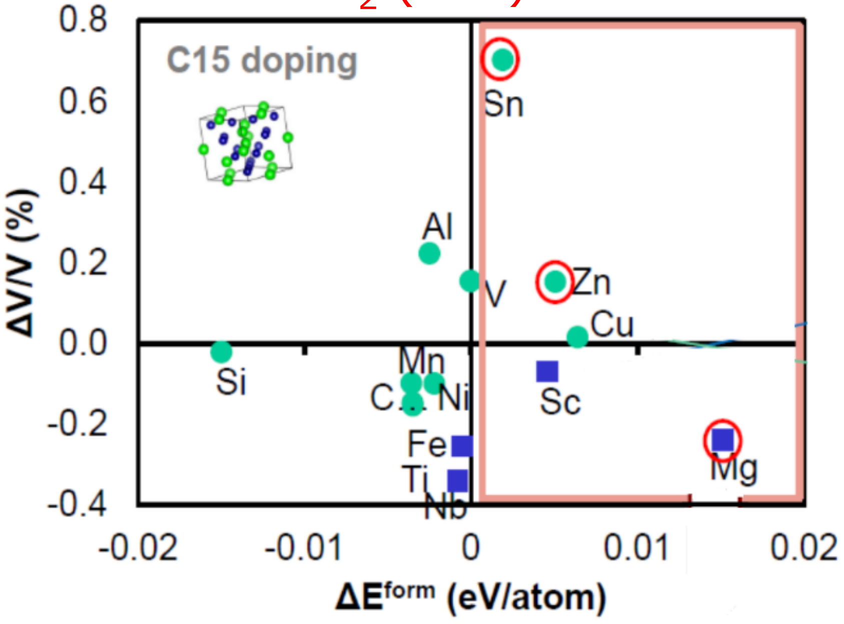
Al
stable in both C15 and Cr, but
$\Delta E_f(Cr)$ slightly $< \Delta E_f(C15)$,
more like Al in bcc-Cr.

X in hcp-Zr

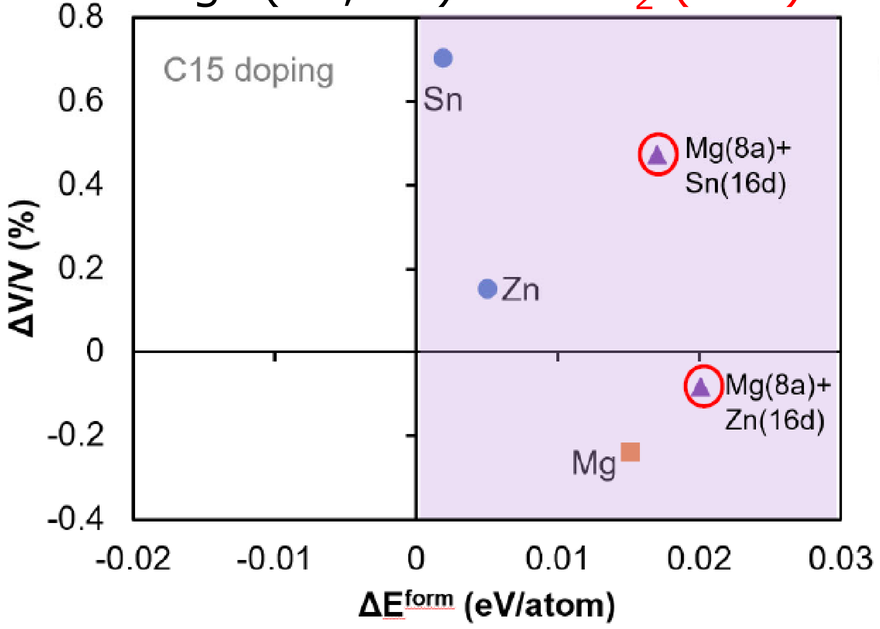


Supercell 3x3x3 bcc cells (54 atoms)
doping concentration 1.85%

X in $ZrCr_2$ (C15)



Mg+(Sn, Zn) in $ZrCr_2$ (C15)



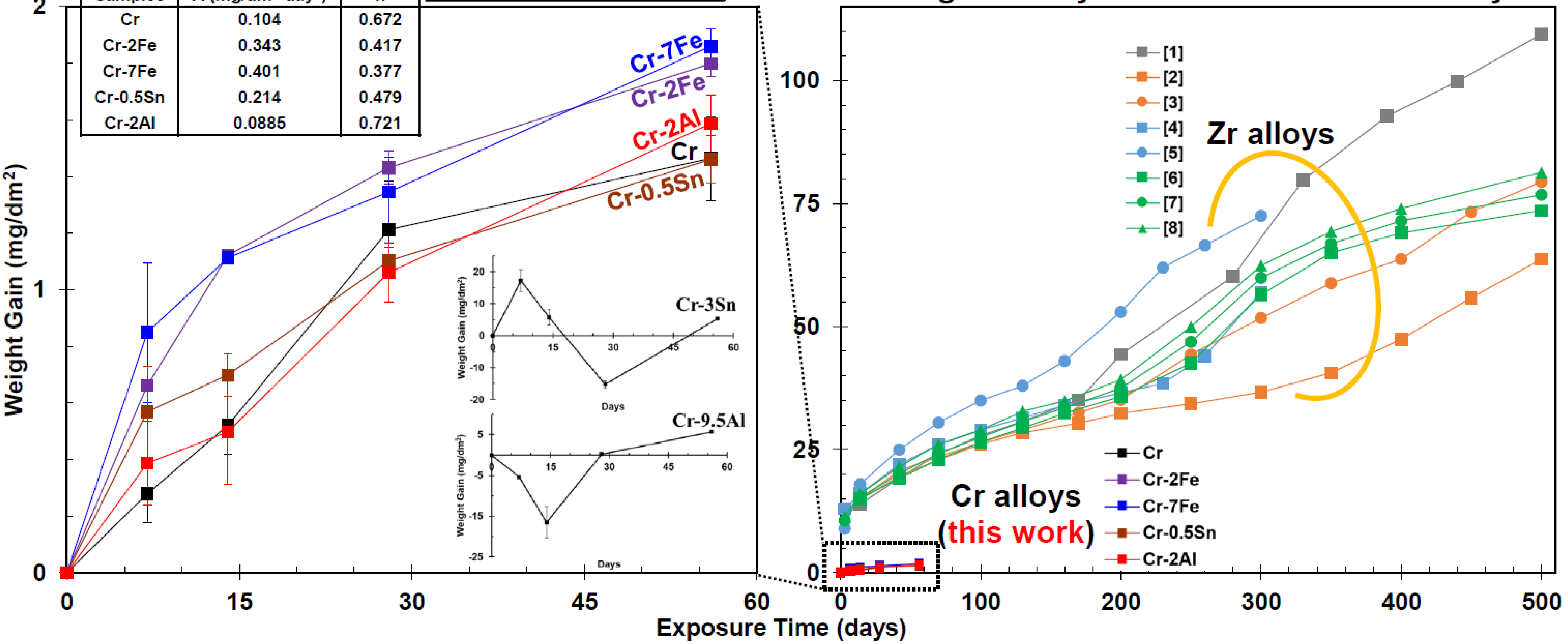
耐食性

Oxidation law [ref 1] constants A and n.

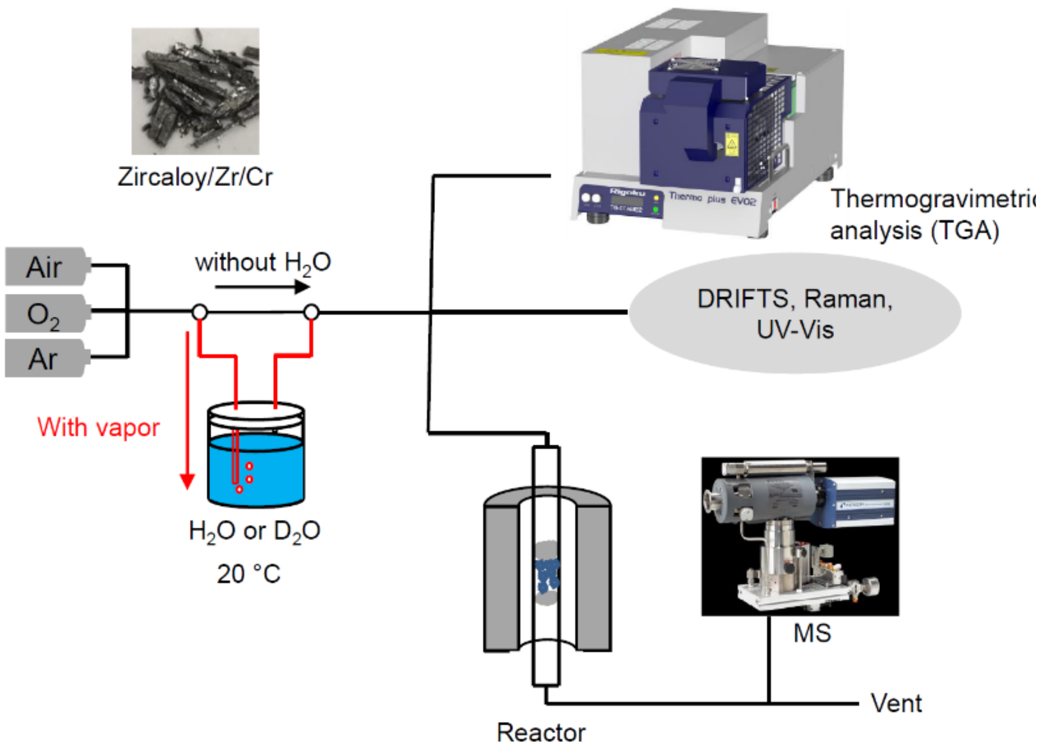
Samples	A (mg/dm²-dayⁿ)	n
Cr	0.104	0.672
Cr-2Fe	0.343	0.417
Cr-7Fe	0.401	0.377
Cr-0.5Sn	0.214	0.479
Cr-2Al	0.0885	0.721

$$\Delta w = (k_p t)^n = A(t)^n \quad (6)$$

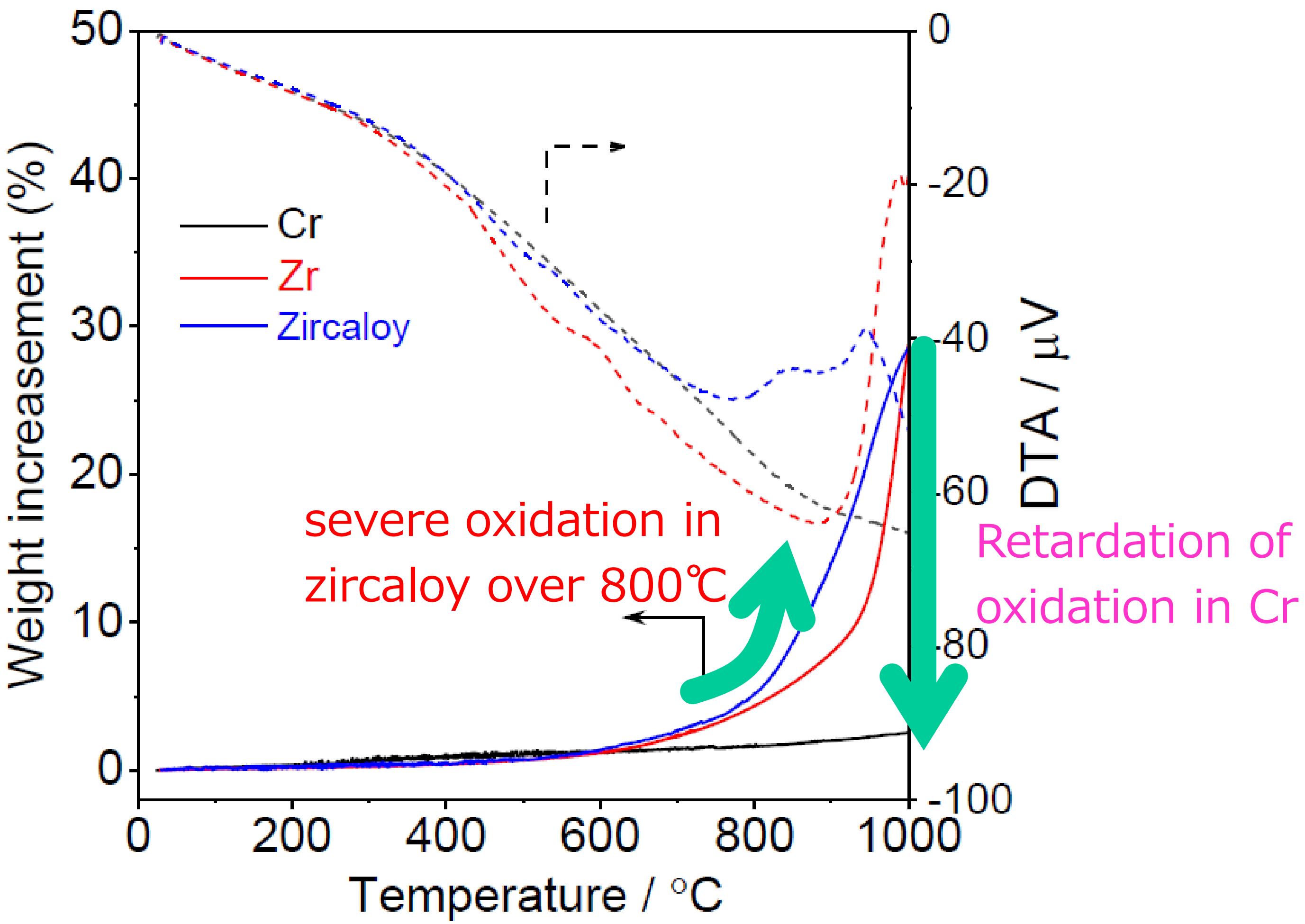
Corrosion weight gains of Cr alloys (this work) are significantly lower than those of Zr alloys!



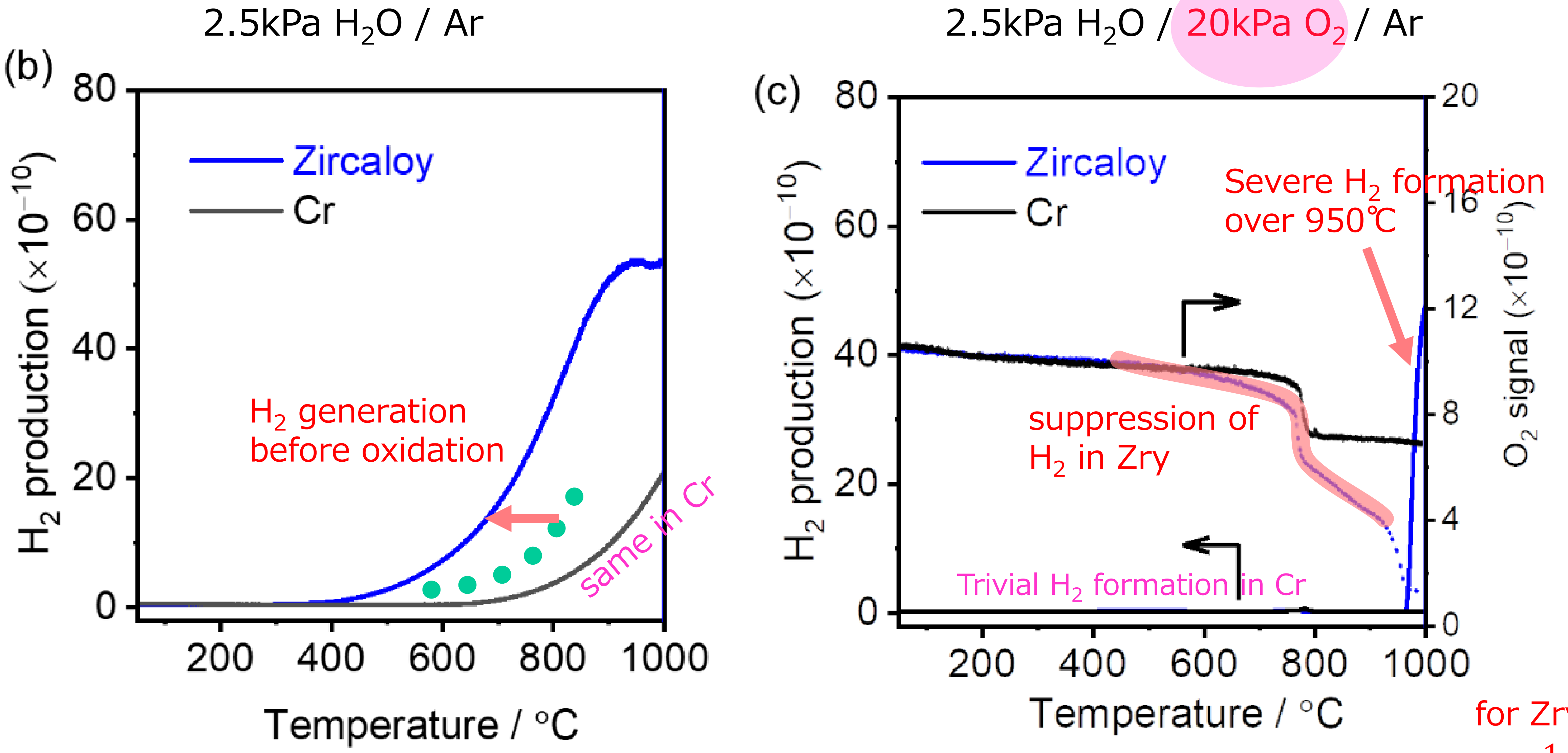
Cr－水反応



Weight: 15-20 mg; Ramp: 5 K min^{-1};
Condition: 20 kPa O_2/2.5 kPa H_2O/Ar



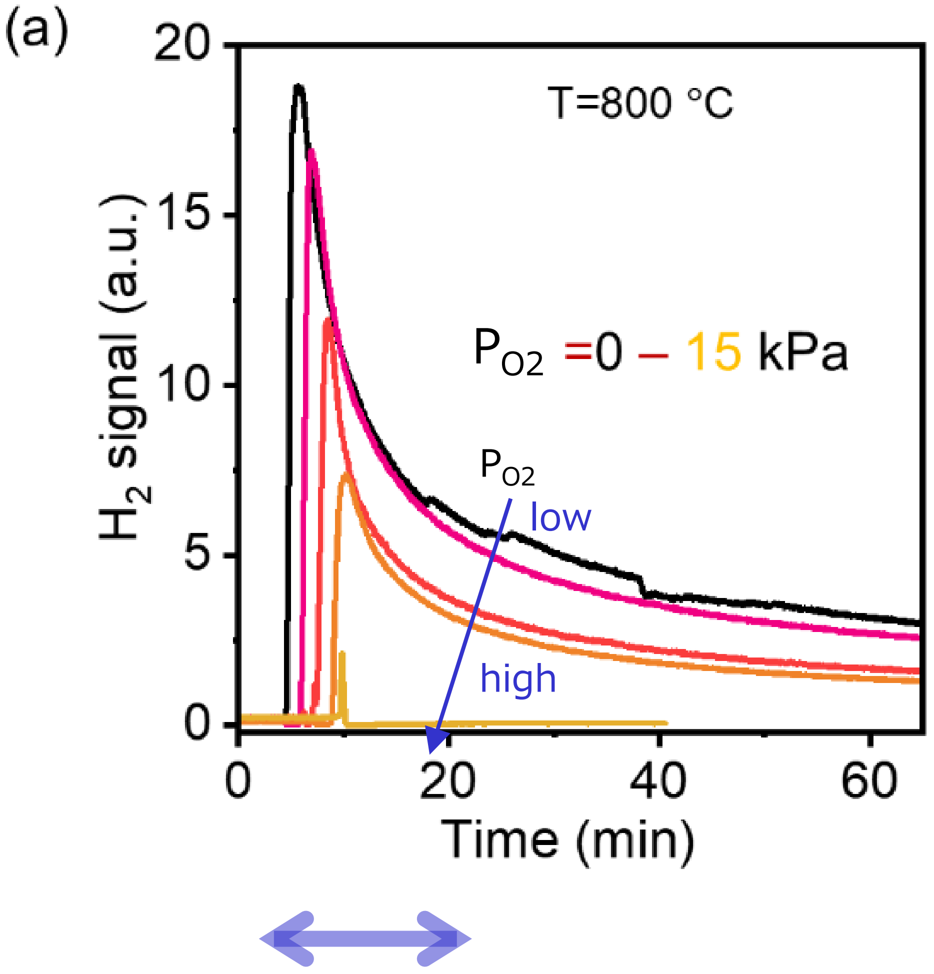
水素発生とその抑制



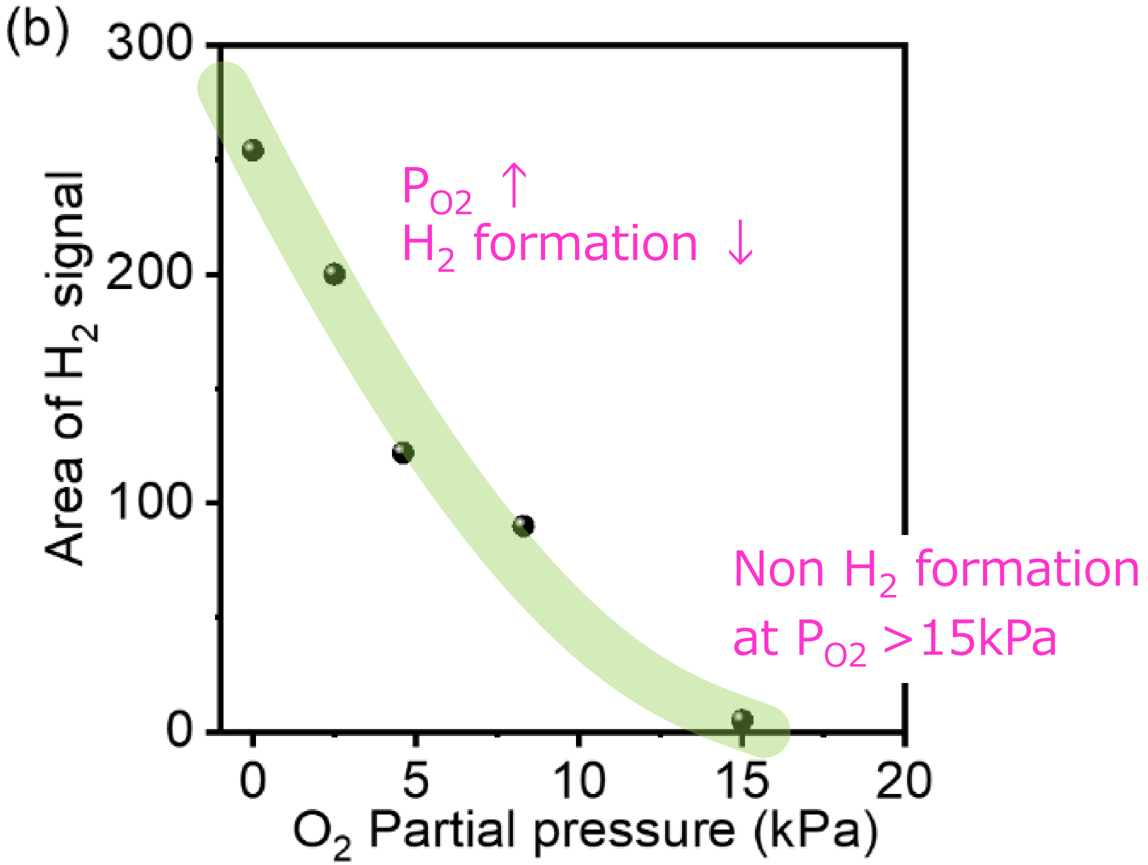
H_2 formation by catalytic reaction
without surface severe oxidation

Mixture of O_2 suppress H_2 formation $\leq \frac{1}{10}$ for Zry

残留酸素による水素発生の抑制

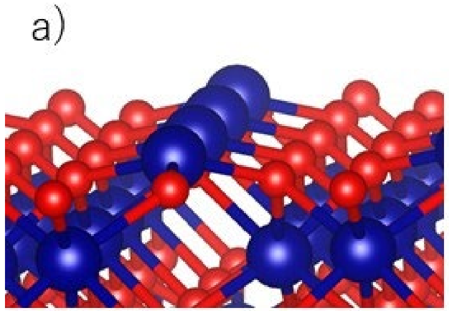


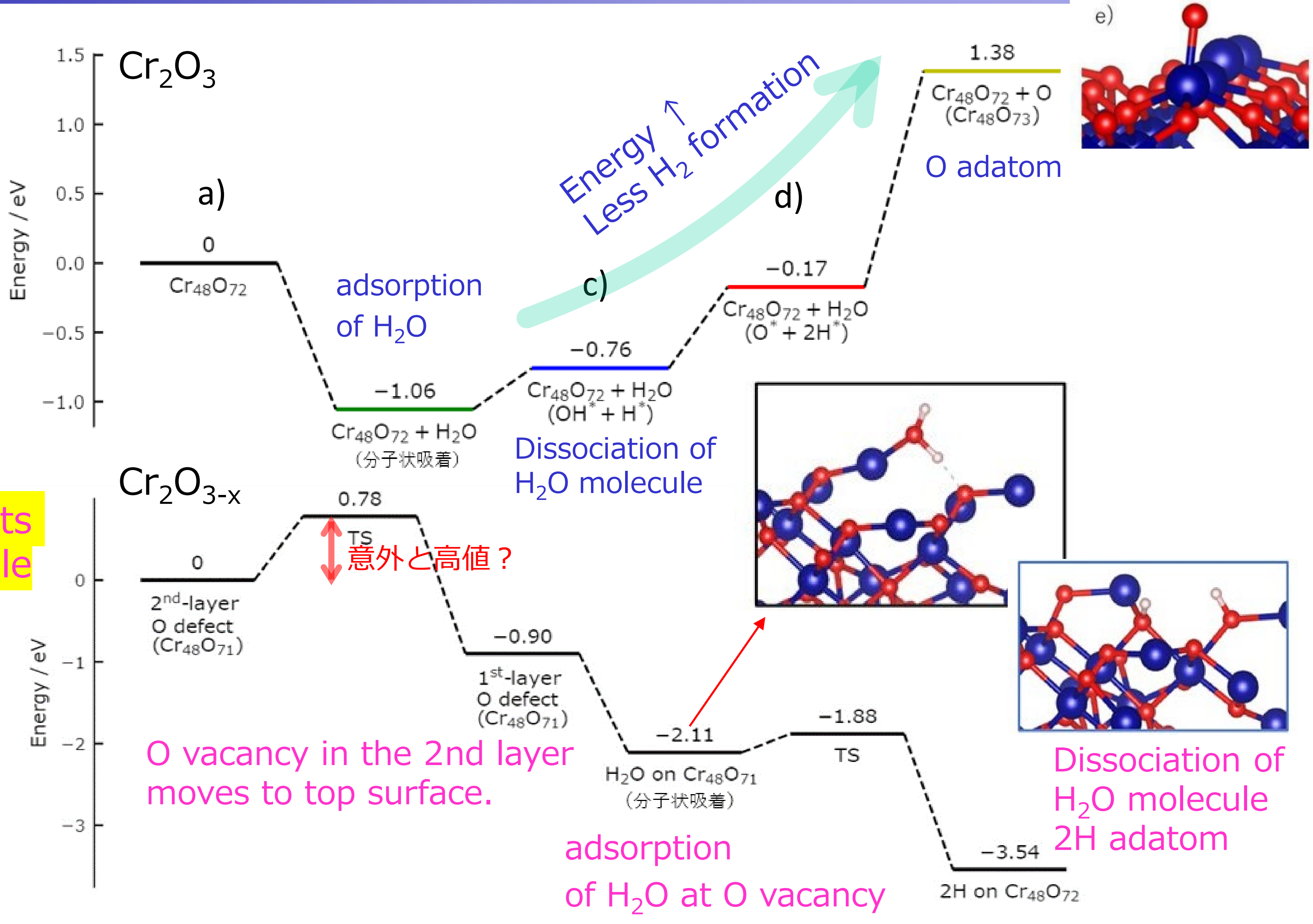
H$_2$ formation is limited at the beginning of exposure
→ suppression by Cr_2O_3 layer formation



O_2 gas in environment suppresses H_2 formation

水素発生に対するCr_2O_3表面酸素空孔の効果





O-vacancy on surface assists dissociation of H_2O molecule

Cr/zircaloy接合

Needs

・joining in the α-phase of Zry

→ Low temperature joining

Concept of exp steps

・diffusion bonding

→ Cr/Zry interface

→ clarify the reaction

- β-phase → accidental condition of NPP
- α-phase → normal operation condition

・application of pulsed laser deposition for low-T joining

→ Developing fabrication concept

introducing excess vacancies to enhance diffusion/mixing

non-equilibrium phase formation to achieve recrystallization at low-T

接合実験

sample preparation

optical grade finish

laser ablation

deposition <100nm

diffusion bonding

duration 4h
at various T

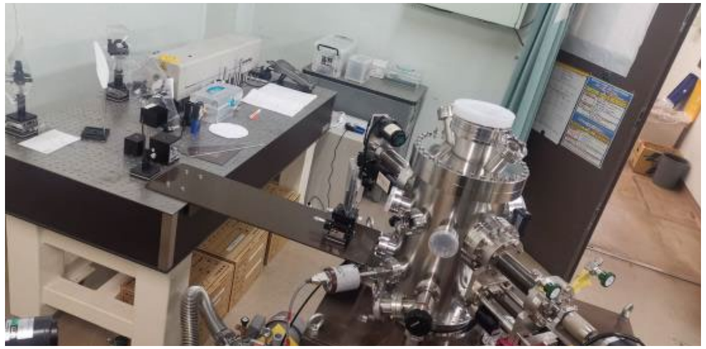
analysis

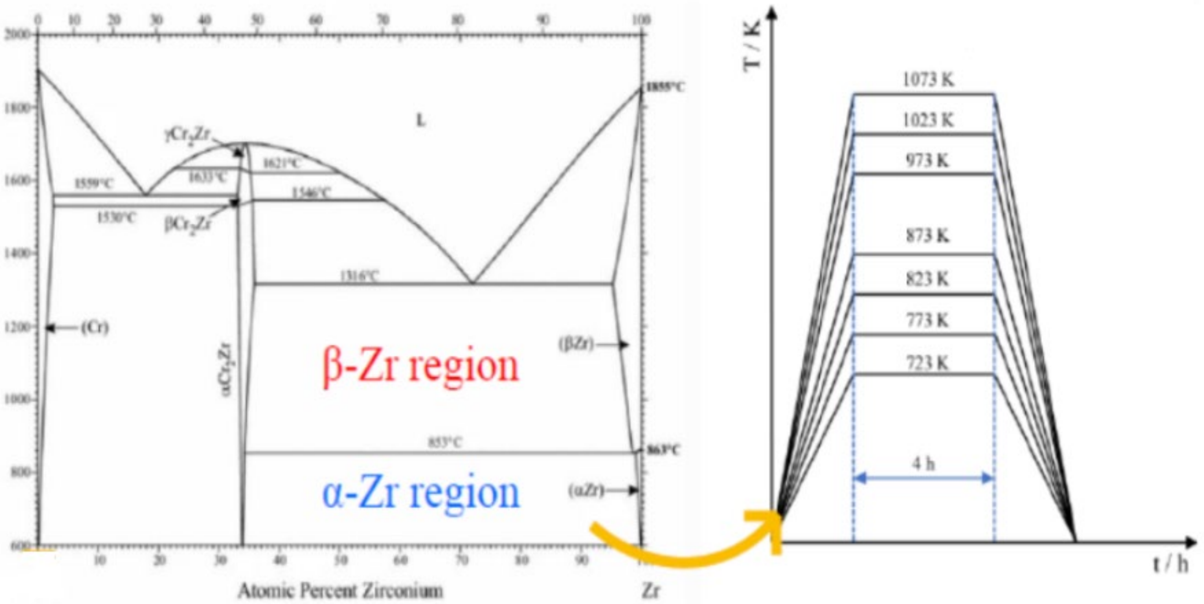
SEM/EDS

FIB/TEM

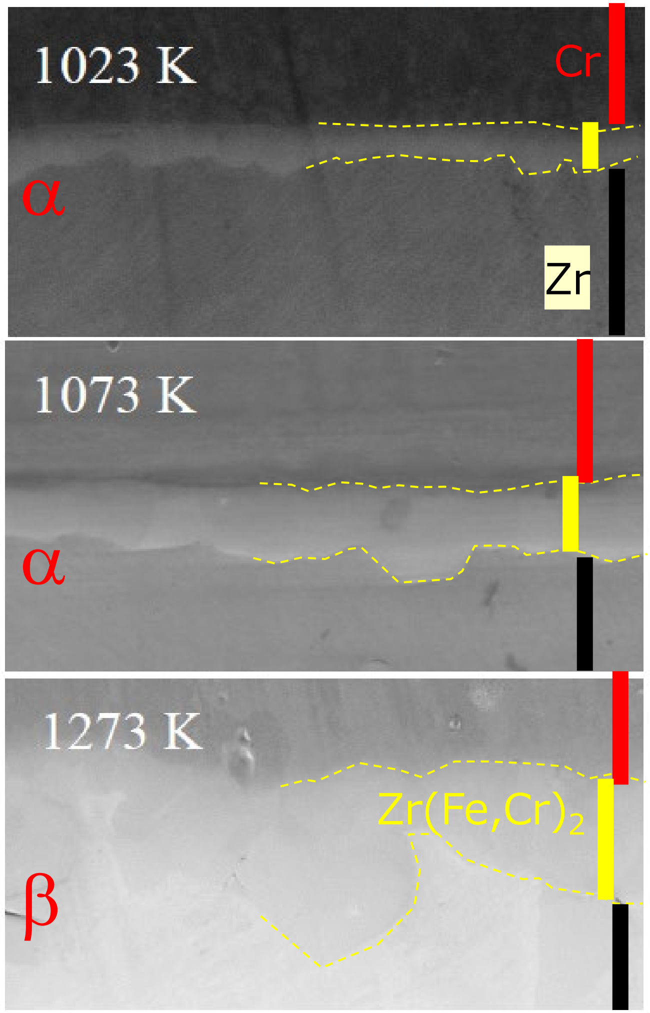
Composition (Wt. %)

Materials	Cr	Fe	Sn	Zr
Cr	99.9	-	-	-
Zry-4	0.07~0.13	0.18~0.24	1.2~1.7	Bal.

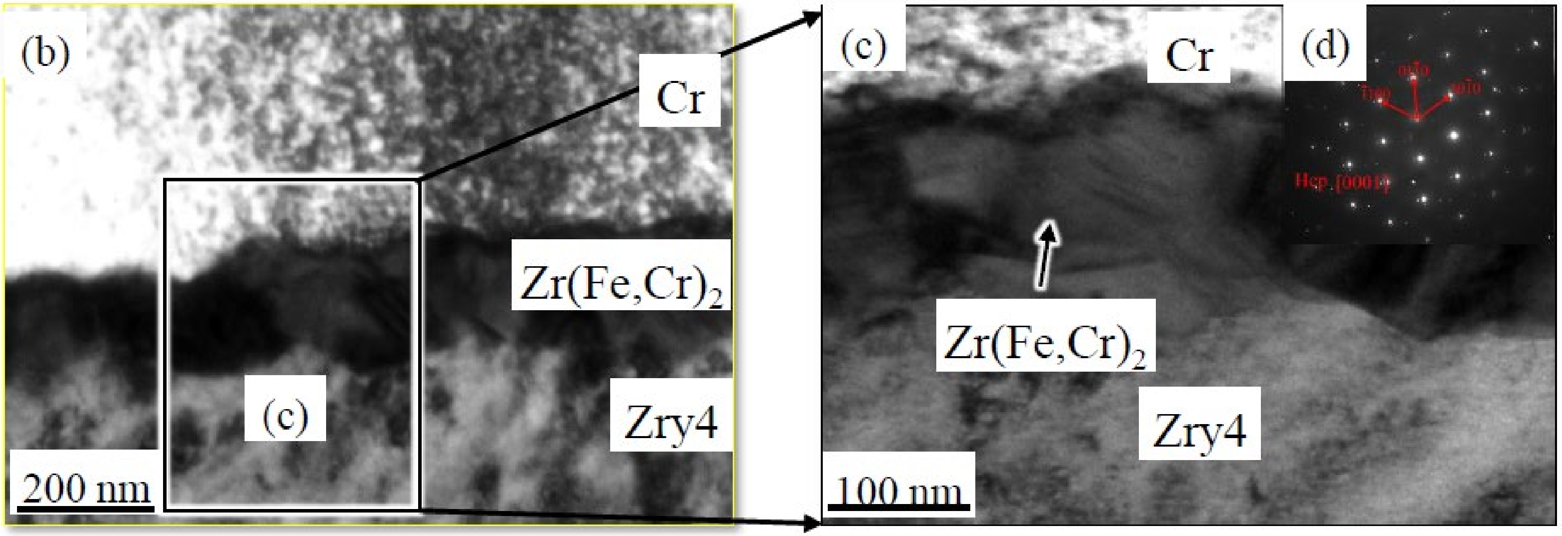


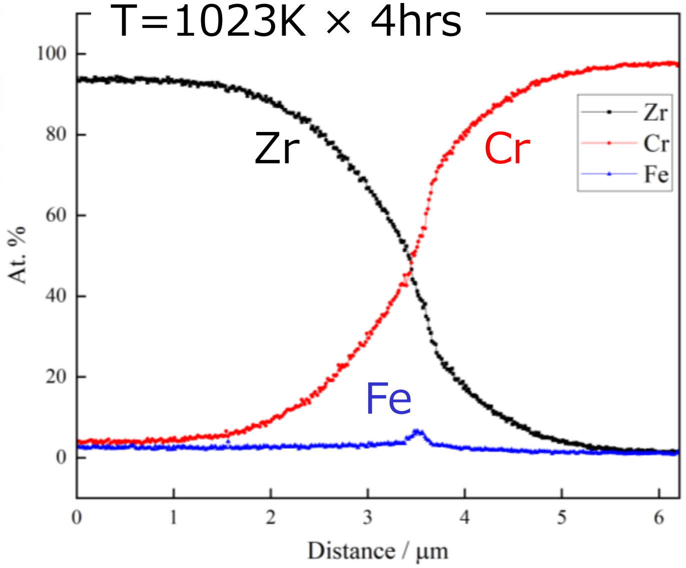


拡散接合によるCr/Zry界面反応：Laves相 $Zr(Fe,Cr)_2$の形成



T=1023K × 4hrs



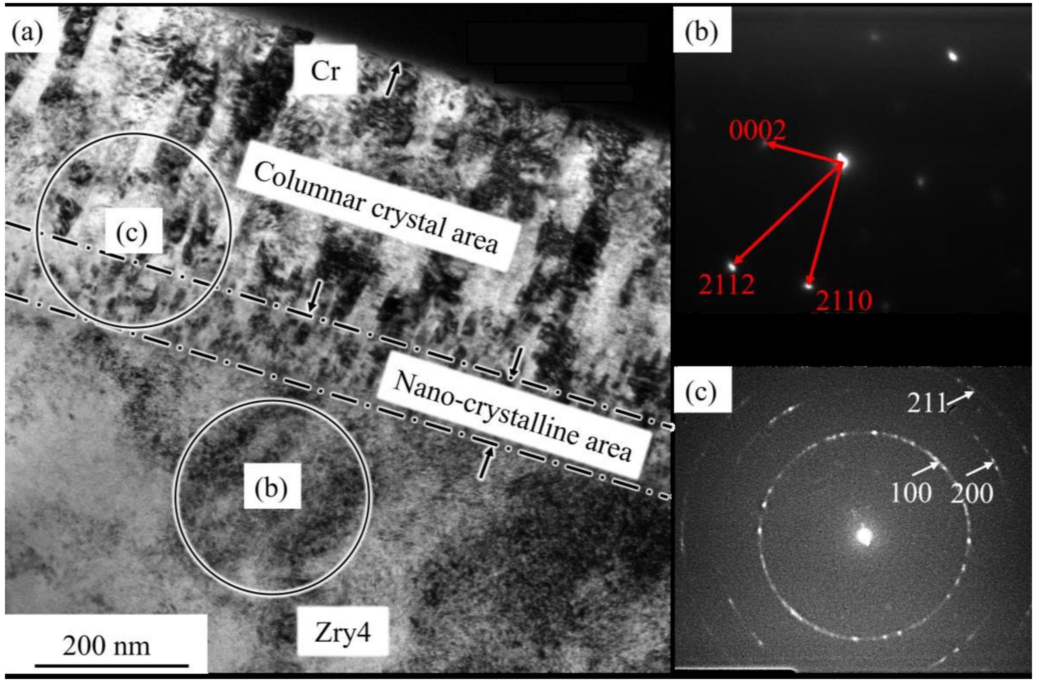


- Preferential diffusion of Cr
- Laves phase layer at interface
- Segregation of Fe
- Bonding at β-phase results in the growth of Laves phase.

パルスレーザー蒸着（PLD）法の応用

Cross section TEM of

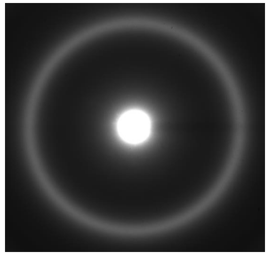
Cr deposited Zry at ambient temperature



Nano crystalline layer formation

Recrystallization temp. >400℃

Amorphous layer formation was observed at shorter or milder deposition.



Recrystallization temp

300～400℃

Idea

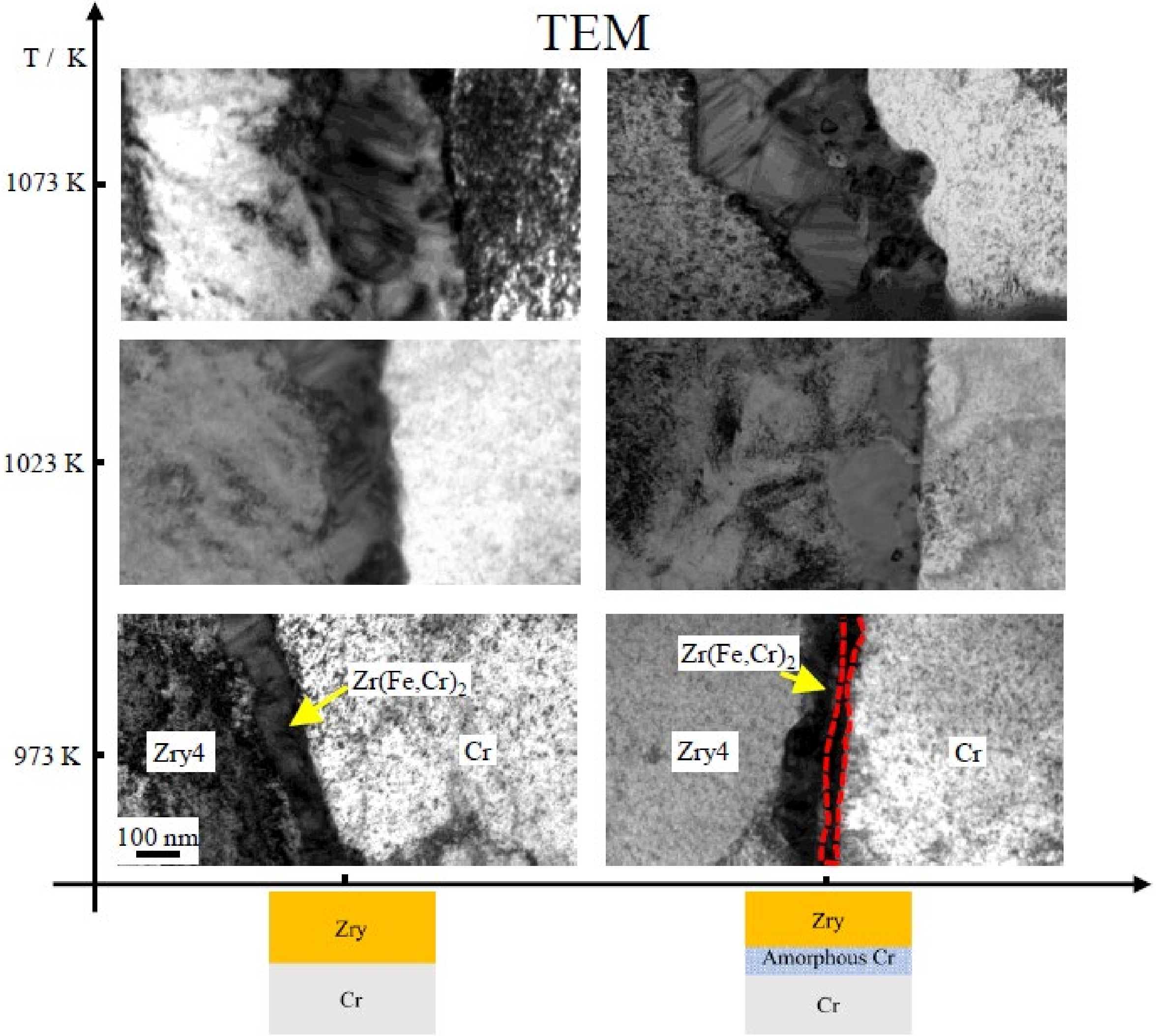
Employ amorphous layer as the buffer layer at the Cr/Zry interface results in

- lower bonding temperature AND
- flatness improvement

PLD法による低温拡散接合

Temp（K）	w/o PLD-Cr	w PLD-Cr
1073	○	○
1023	○	○
973	○	○
873	○	○
823	×	
773	×	○
723		×

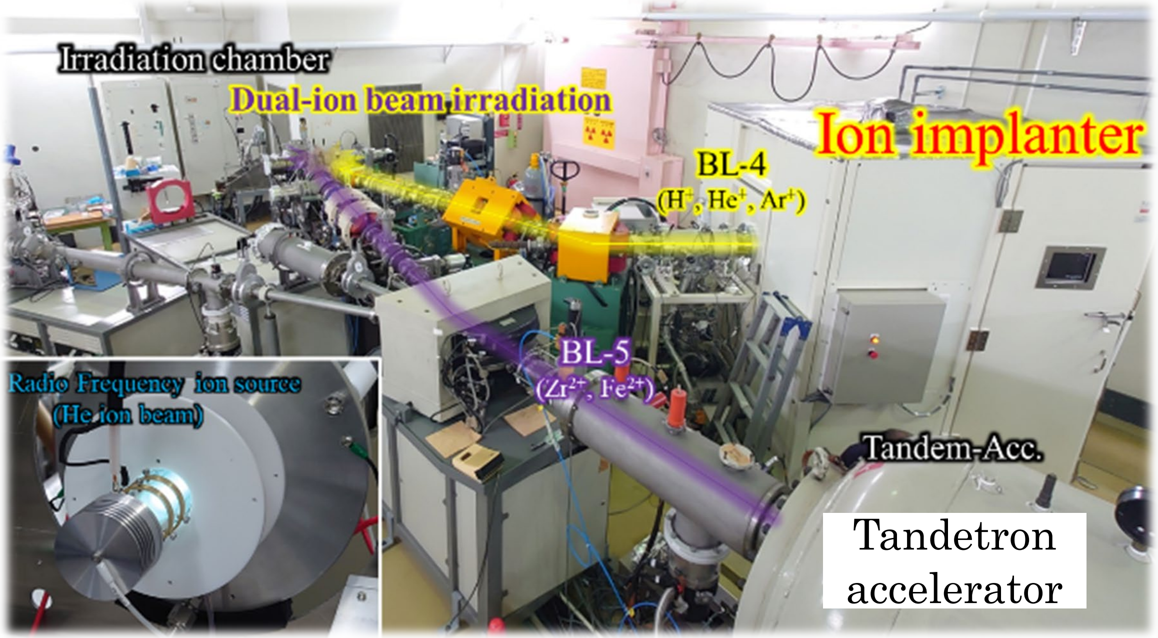
×4hrs



The amorphous layer seems less effective to the formation of Laves phase.

照射影響

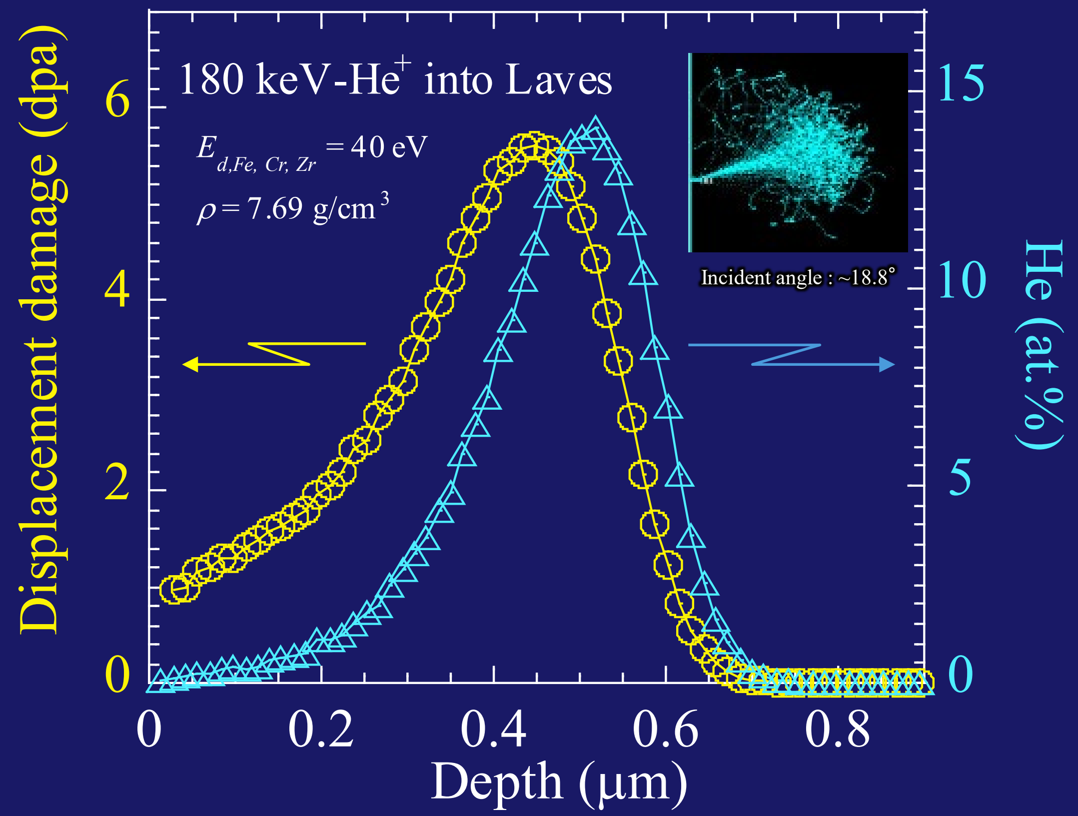
HIT, The Univ. Tokyo



試料作製
arc melting + anneal.

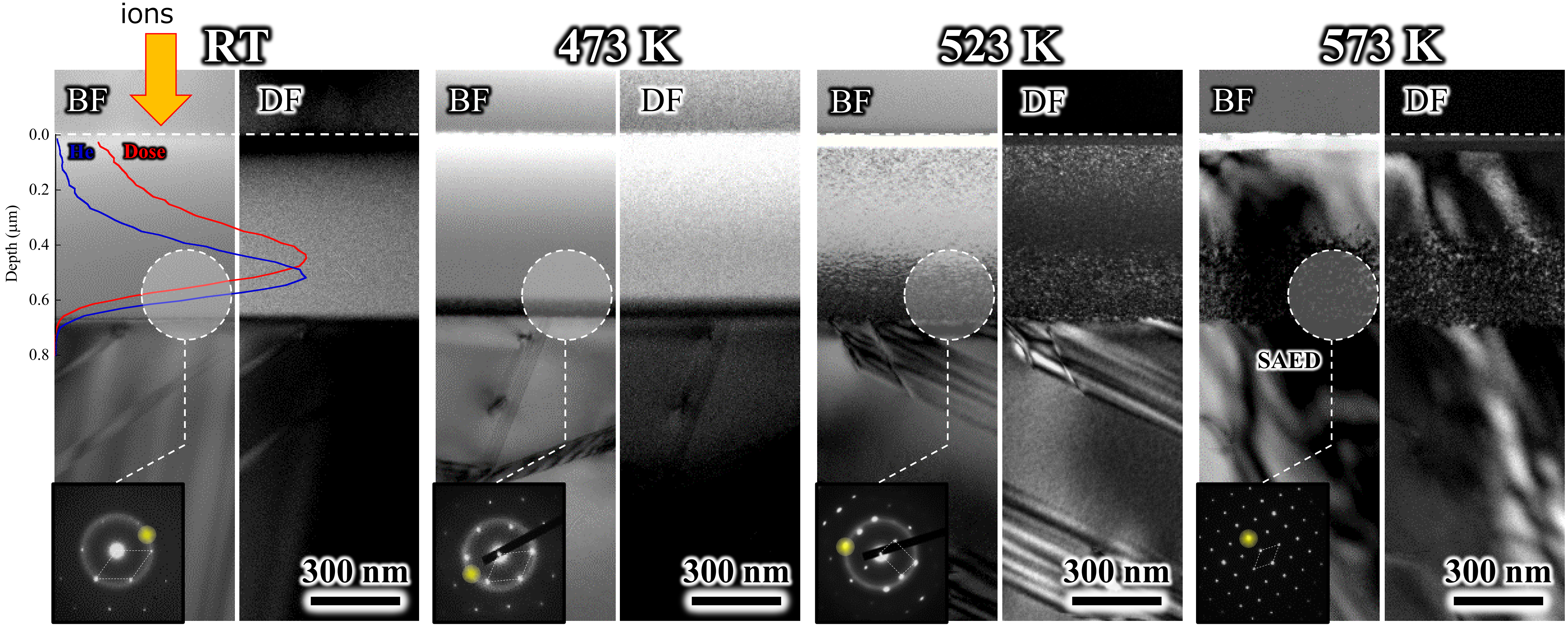
照射後分析
GIXRD
SEM/EDS analysis
FIB and TEM analysis
nano-hardness

Ion irradiation (180 keV-He$^+$, 5.5 dpa @ peak)
Temp.: RT, 473, 523, 573 K

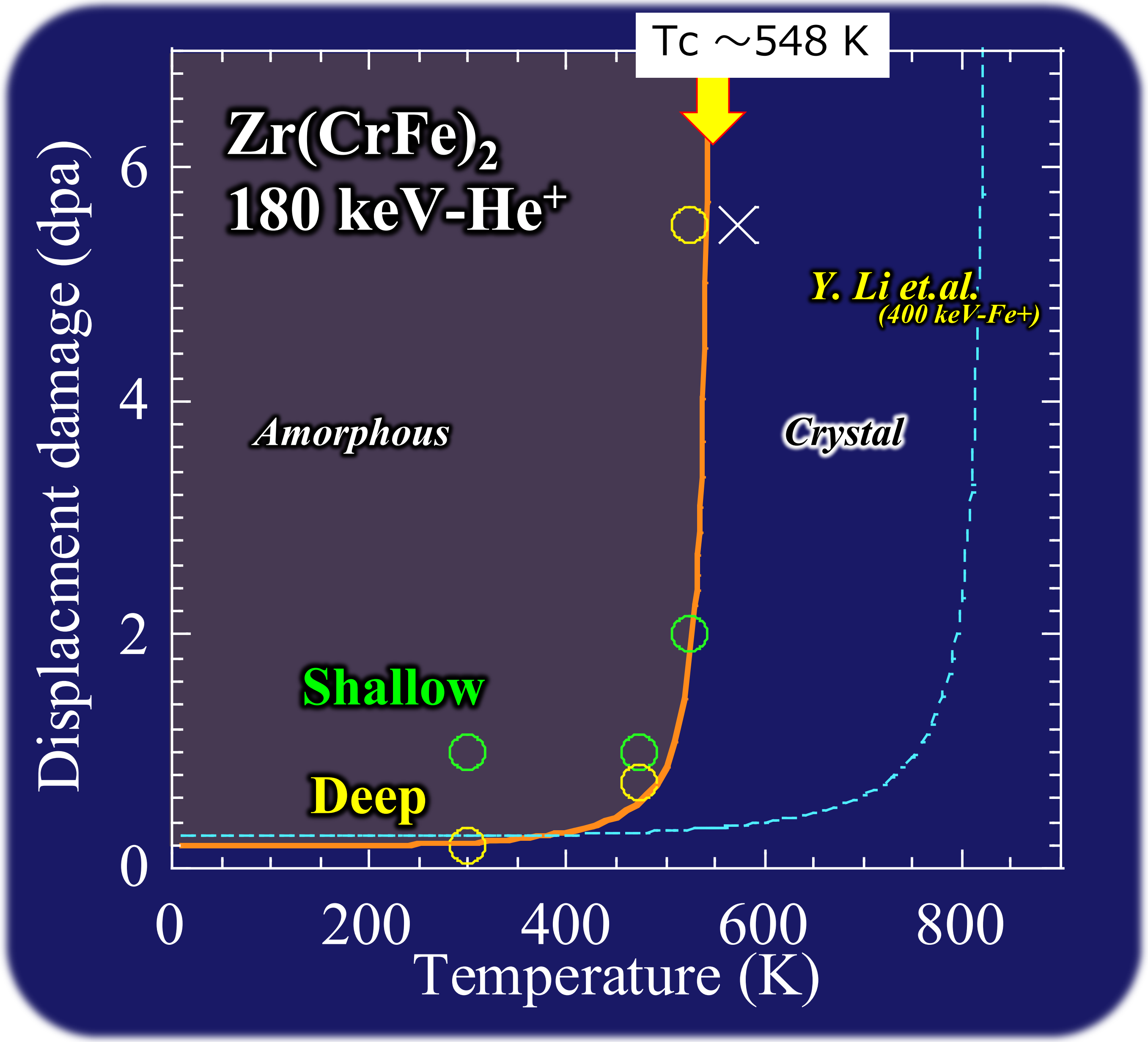


Laves相 $Zr(Cr,Fe)_2$ の照射誘起非晶質化

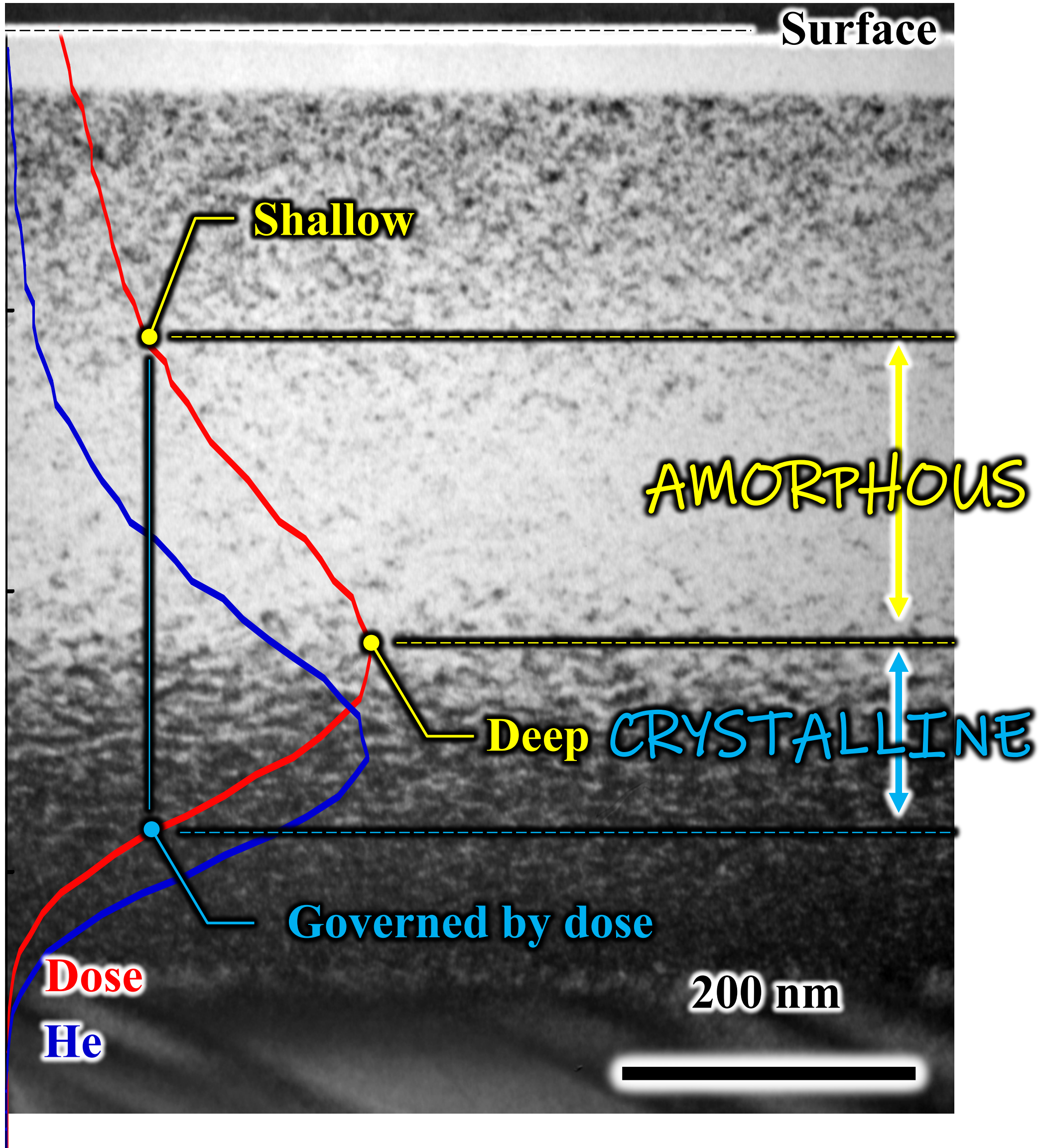
180keV He → $Zr(Cr,Fe)_2$ 5.5 dpa (peak)



Laves相 $Zr(Cr,Fe)_2$ の非晶質化臨界線量



BF, 180keV-He⁺ @ 523 K



Crのイオン照射損傷

Irradiation → FIB and TEM

2.8 MeV Fe^{2+}

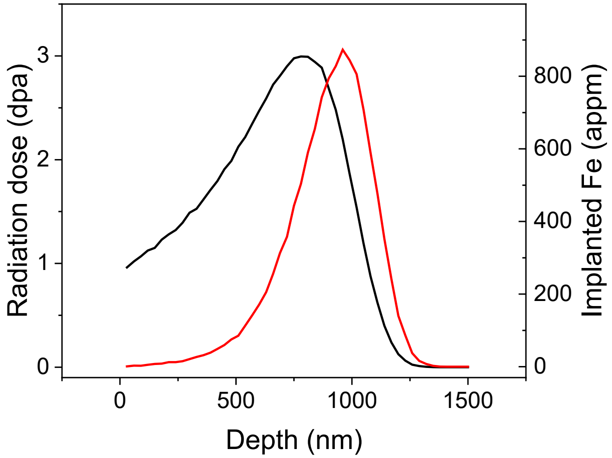
Dose rate 2.1×10^{-3} dpa/s

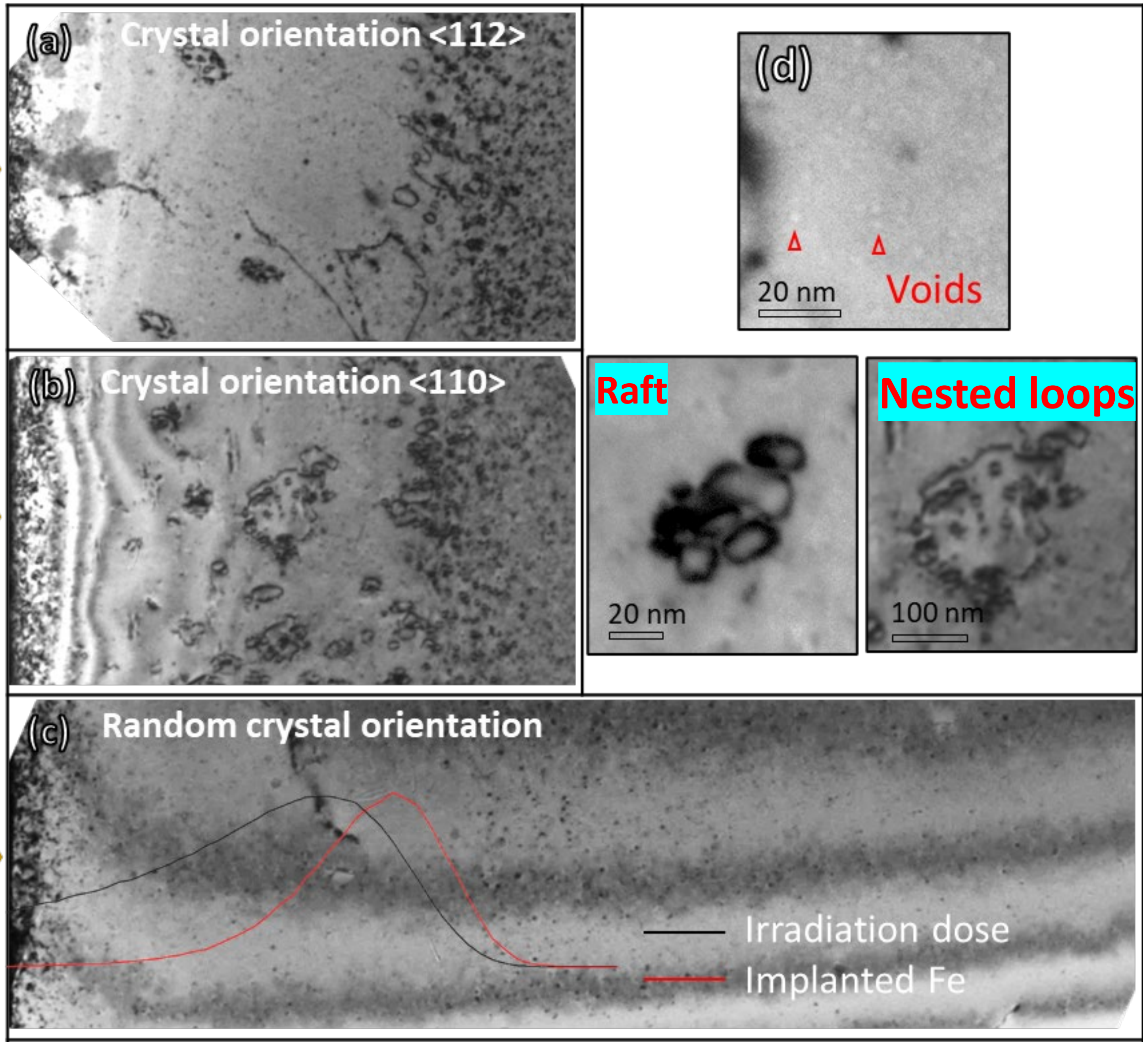
Irradiation flux $2\times10^{12}/cm^2$

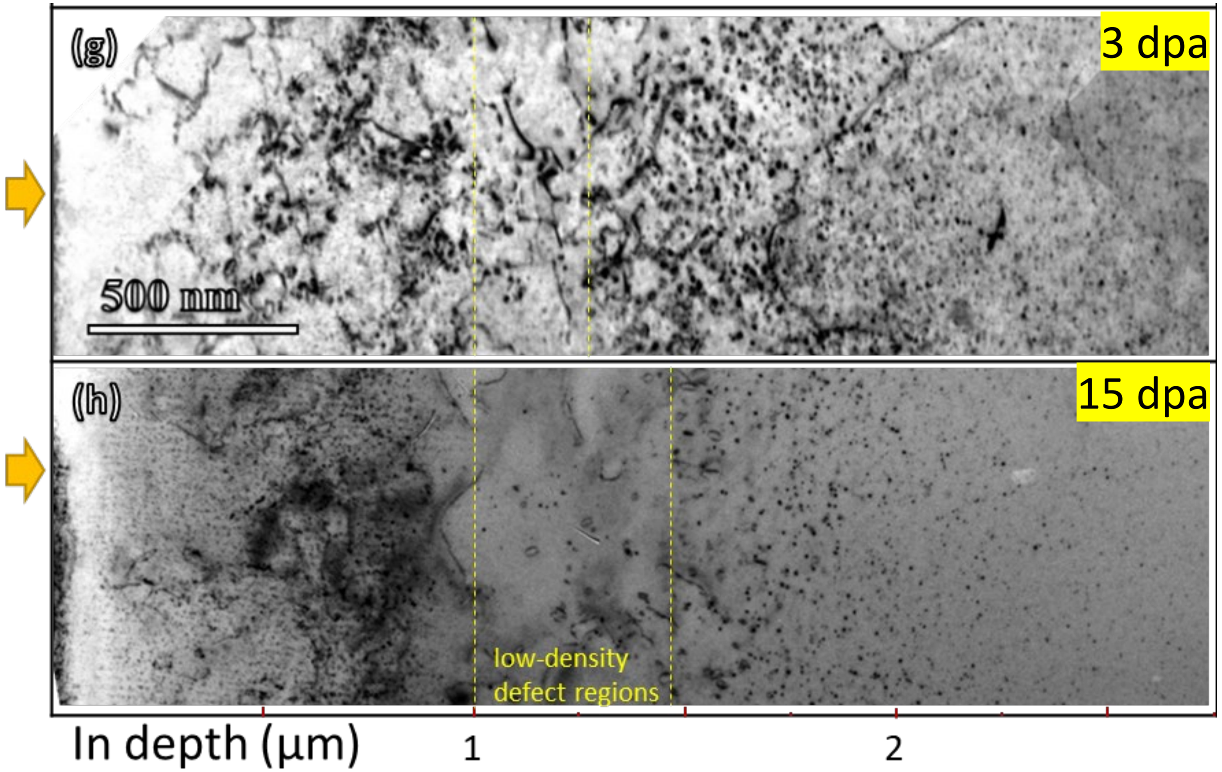
Dose: 0.1 dpa, 3 dpa, 15 dpa

target: pure Cr

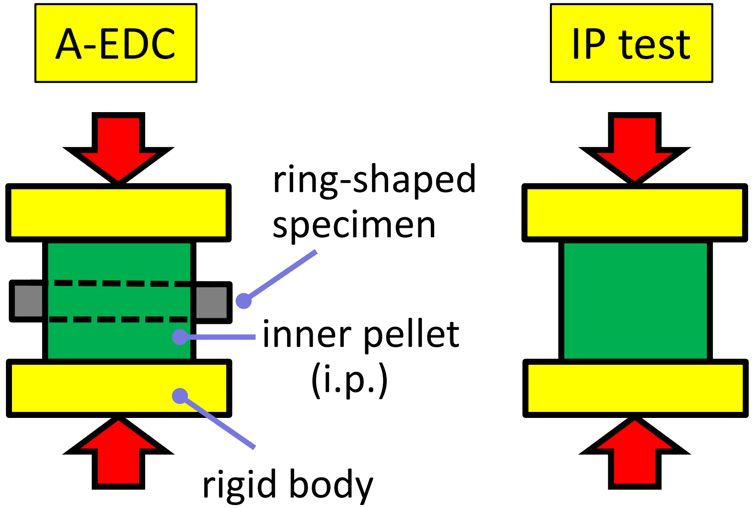
Temperature 550±2 ℃

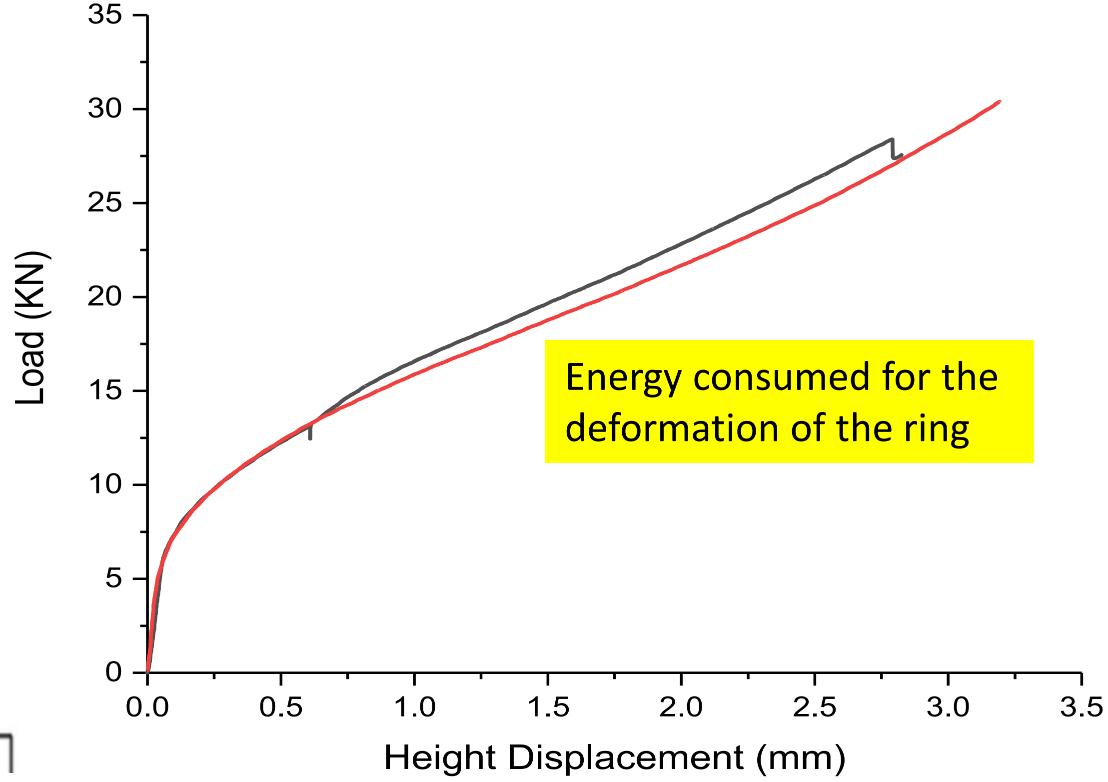


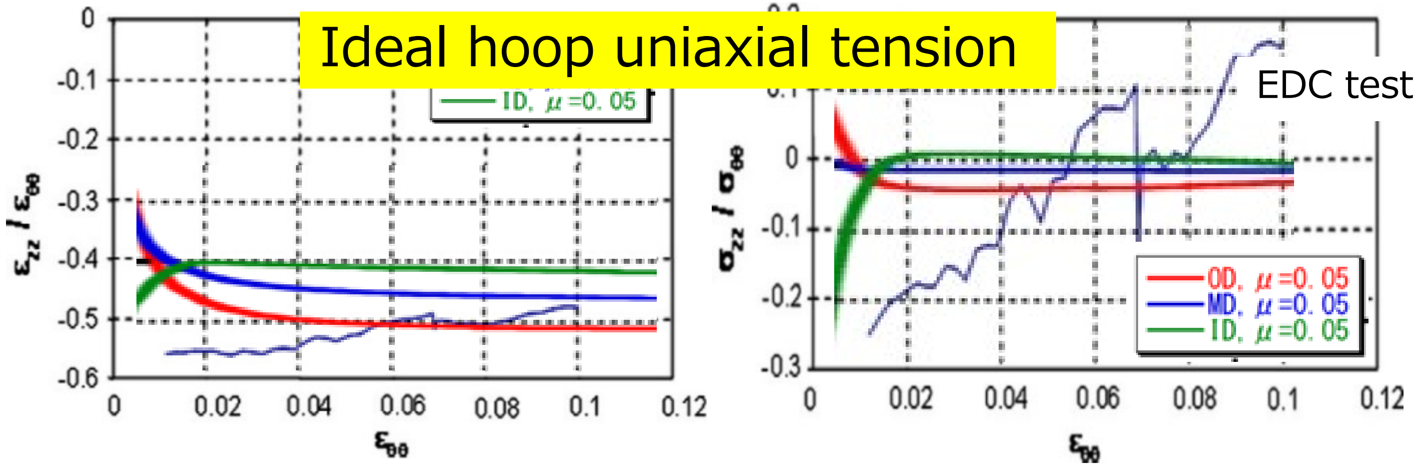




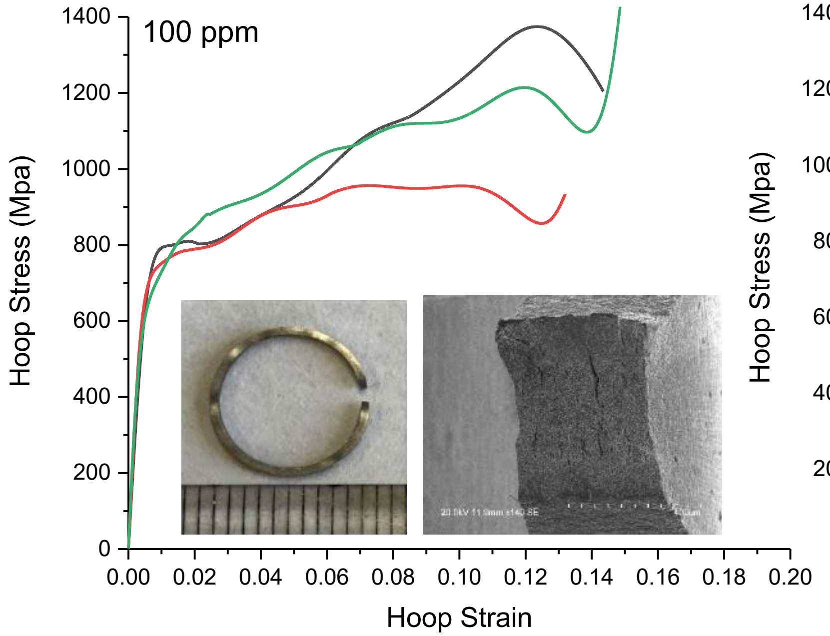
機械試験 (Advanced Expansion Due to Compression (A-EDC) test)

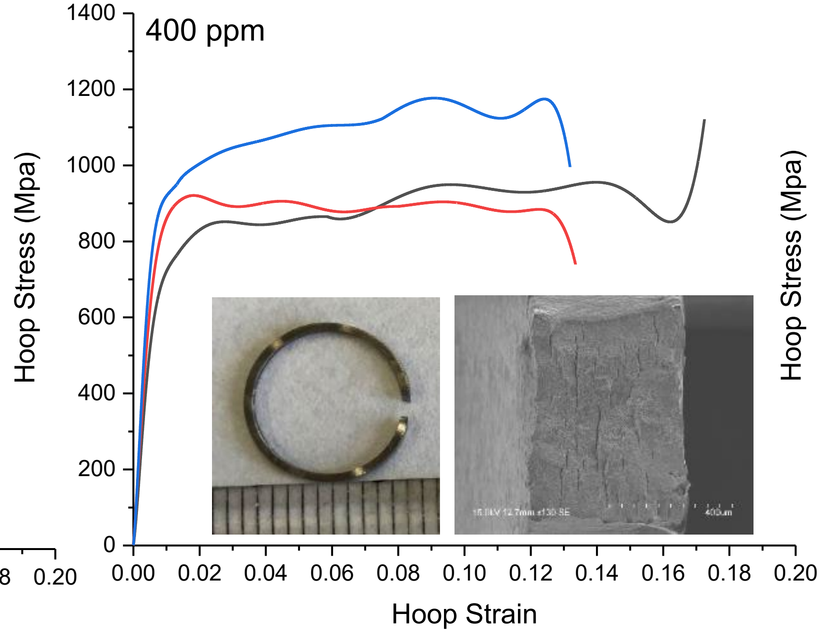


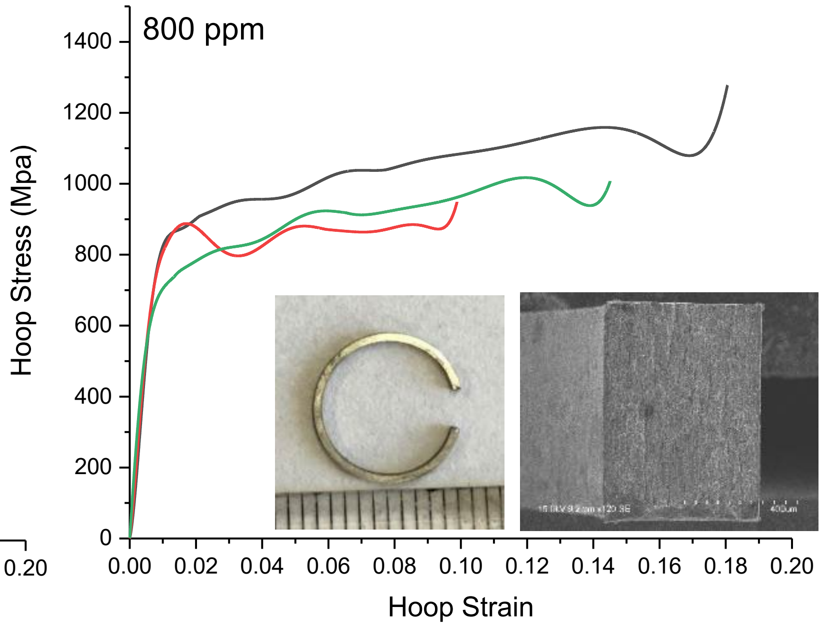




水素吸収効果（Zircaloy-4）







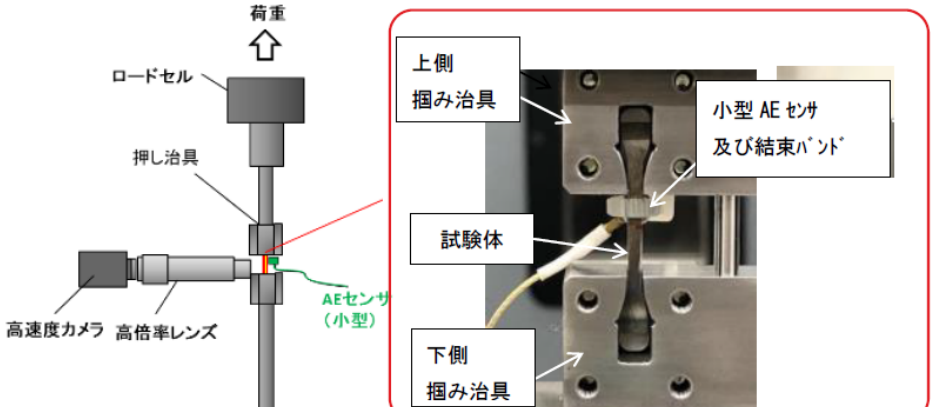
Hydrogen content [ppm]	Yield Stress [MPa]
0	899± 40
100	801± 8
400	1010± 77
800	912±122

σ_y increased due to H

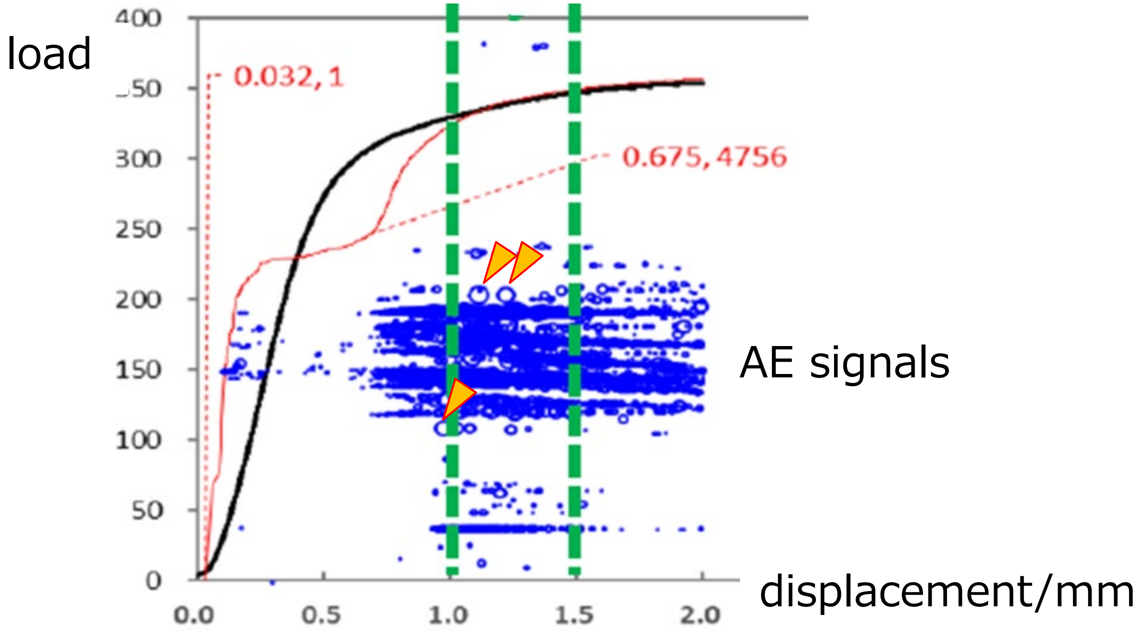
- Multiple necking observed.
- Necking become shallower with increasing the with increasing the hydrogen content.
- Fewer necking was evident in 800ppm.

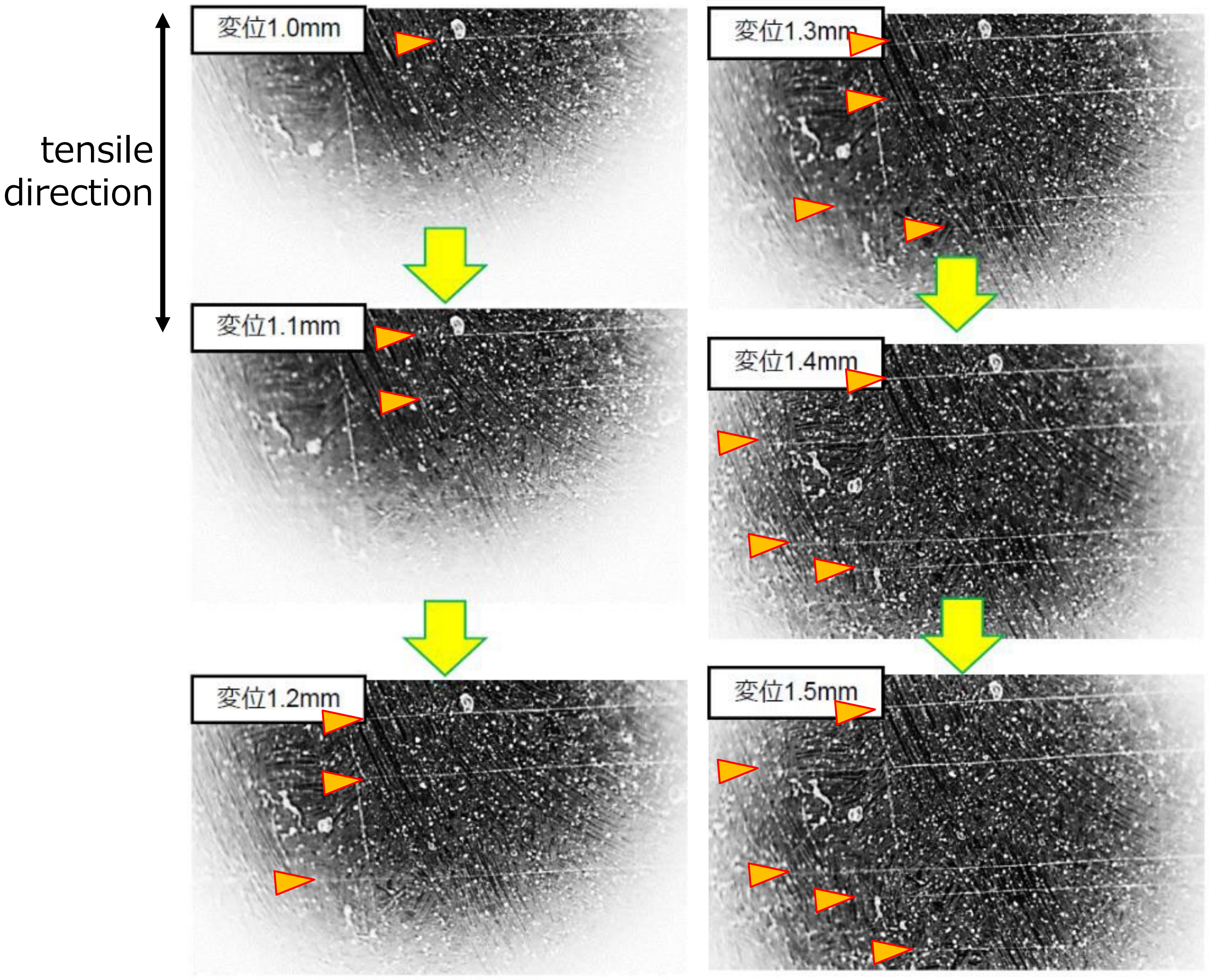
Due to the texture structure of zry, platelet hydrides are formed along hoop direction. Less effective to the hoop strength.

Cr被覆Zry-4の曲げ試験とその場測定



High speed camera is set for in-situ obs. in bending/tensile.
AE sensors for detection of crack formation.





Crack formation and propagation on Cr side.
AE detected the formation.

まとめ、総合討論

- Cr/Zry接合に成功した。界面反応による層状のLaves相形成を確認した。
- バッファ層として非晶質Crを用いることにより接合の低温化に成功した。

Crコートジルカロイ被覆管について、本研究成果より以下の提案がなされる。

- 製造工程においては界面に非晶質相を形成させることにより、より低温での接合性を期待することができる。
- ただし、熱処理温度次第でキャビティの形成（未説明）も観察されたことから、熱処理条件には注意が必要。
- 異常条件では、界面にLaves相が層状に形成されることから、その影響評価は必要である。これは、製造法によらない。
- Laves相形成は拡散律速であることから、これに対する照射加速影響も懸念され、今後の課題としている。

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阿部弘亨
abe.hiroaki@n.t.u-tokyo.ac.jp