HOKKAIDO UNIVERSITY

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Stability of hydrides and precipitates in Zr alloys under high energy particle irradiation

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The 2nd WS on The Use of In Situ TEM / Ion Accelerator Techniques in the Study of Radiation Damage in Solids, Albuquerque, New Mexico, USA, June 5-9, 2011

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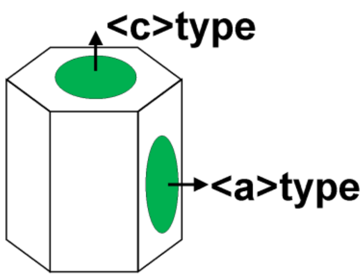
Introduction

Zirconium alloys - Small neutron absorption cross-section

Cladding tube using in light water reactor
Channel box for BWR fuel assembly

1. Radiation damage - Hardening or expansion

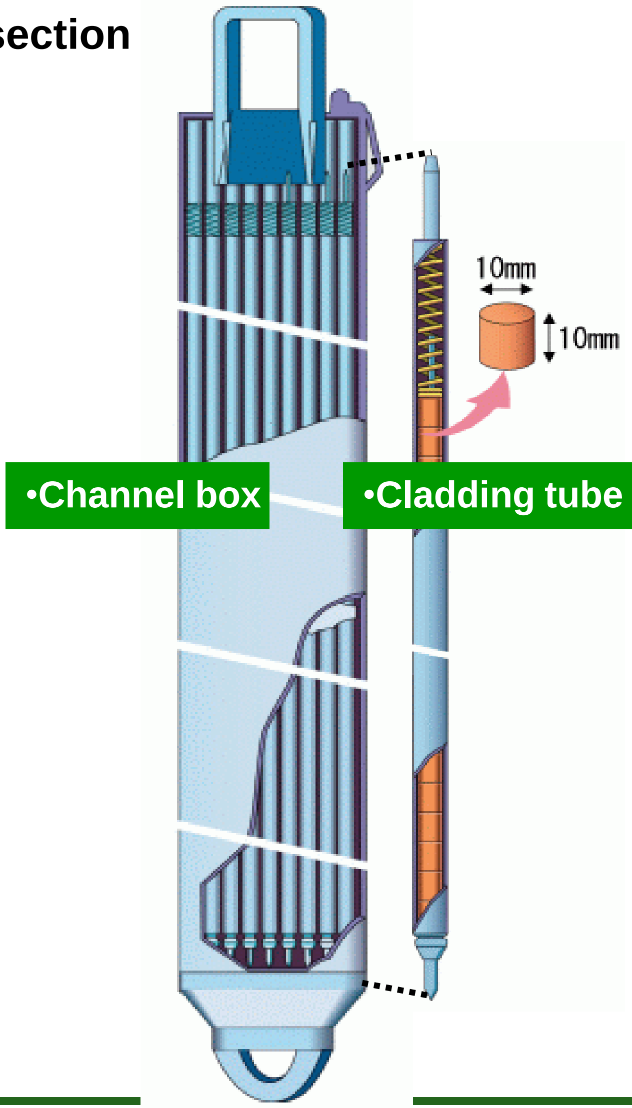
<a> type and <c> type dislocation loop



2. Hydride formation - Hydrogen embrittlement

Irradiation damage structures of Zr materials
Irradiation behavior of zirconium hydride remains to be clarified sufficiently.

BWR fuel assembly



• Agency for Natural Resources and Energy, "Nuclear Power 2009", (2009)

For the basic study of irradiation behavior in Zr alloys

Formation and development of damage microstructure by electron irradiation for Zr, Zircaloy-2 (Zry-2), and Zircaloy-4 (Zry-4)

Irradiation behavior of zirconium hydride by electron irradiation to zirconium hydride in Zr

Experimental - samples and procedure

Samples

Zr: 800 °C, 2h annealed

Zry-2 and Zry-4: as received
(β-quenched → rolled → annealed)

Chemical composition (wt.%)

	Zr	Hf	Fe+Cr	H	N	C
Zr	Balance	< 4.5	< 0.2	< 0.005	< 0.0025	< 0.05

	Zr	Sn	Fe	Cr	Ni
Zry-2	Balance	1.2-1.7	0.07-0.20	0.05-0.15	0.03-0.08
Zry-4	Balance	1.2-1.7	0.18-0.24	0.07-0.13	-

Procedure

Damage structures
- Zr, Zry-2, Zry-4

Irradiation behavior of Hydride
- Zr
- Cathodic hydrogen changing

Preparation for TEM specimens
(punch-out, electrochemical polishing)

Electron irradiation

Experimental - Irradiation condition and hydrogen charging

Damage structures	Irradiation behavior of Hydride
Zr, Zry-2, Zry-4	Zr
	↓
	Cathodic hydrogen changing

↓

Preparation for TEM specimens
(punch-out, electrochemical polishing)

↓

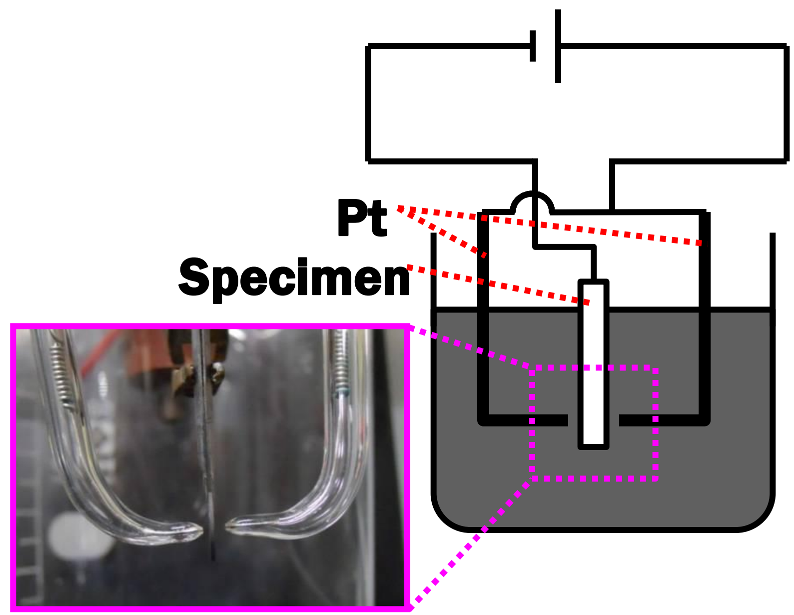
Electron irradiation

Irradiation condition

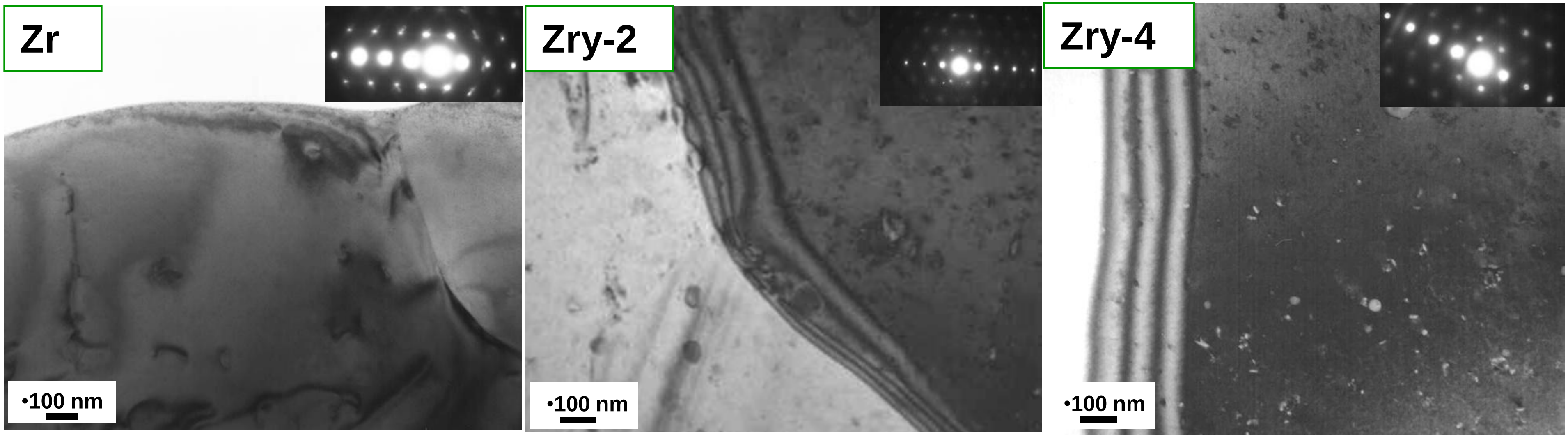
Accelerating Voltage [kV]	1250
Temperature [^oC]	300
Dose rate [dpa/s]	5 x 10^{-4}, 3 x10^{-3}
Maximum dose [dpa]	1~5

Cathodic hydrogen changing

Sample: Zr disk, ϕ10x0.5 mm
Electrolyte: 0.125M H_2SO_4
Current density: 50~100 mA/cm^2
Charging time: 12 h



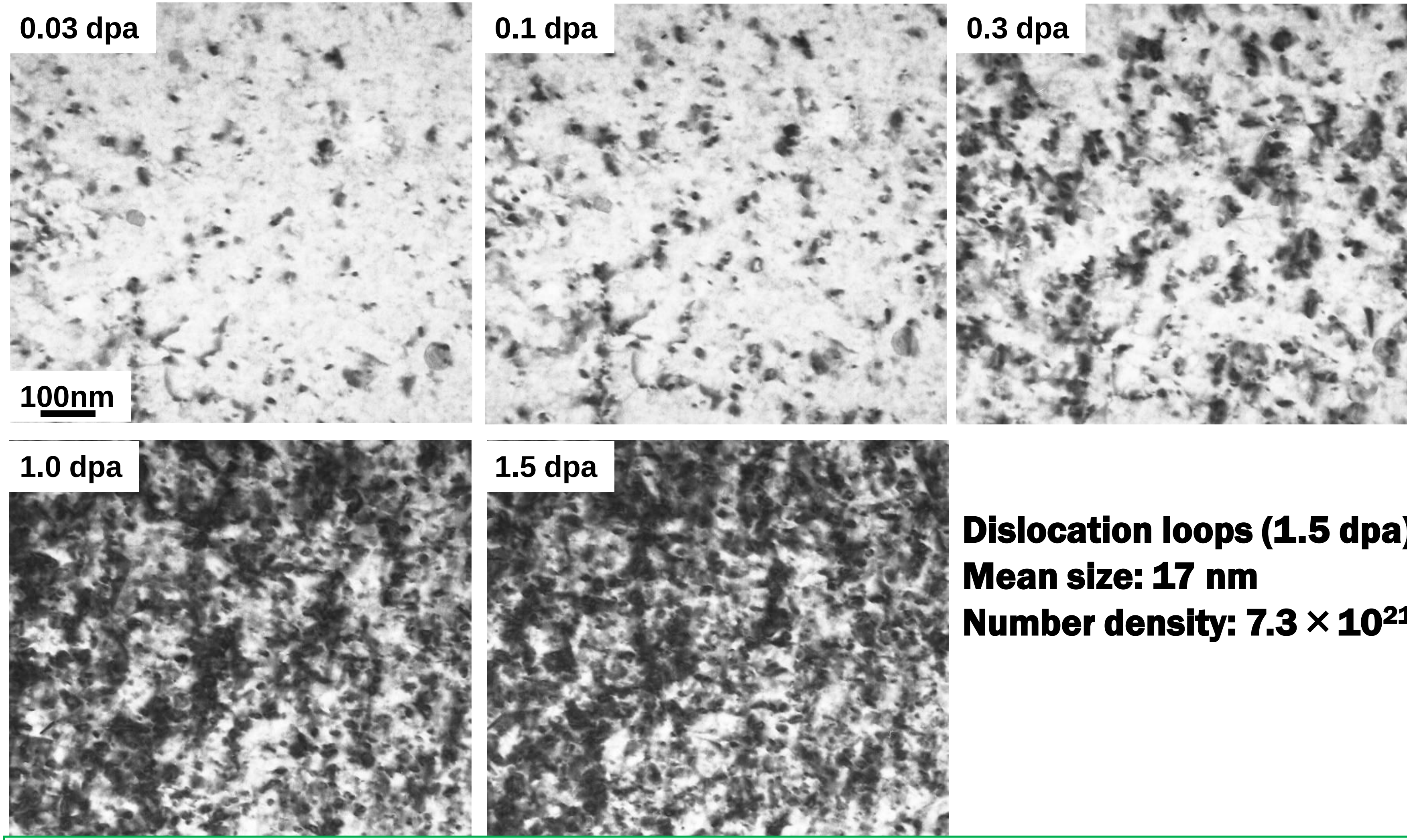
Microstructures of each sample before irradiation



	Precipitates	Size	ND
Zr	-	-	-
Zry-2	○	Mean: 40 nm Max: ~130 nm	3×10^{19} m^{-3}
Zry-4	○	Mean: 40 nm Max: ~130 nm	9×10^{19} m^{-3}

Thickness; 300~500 nm

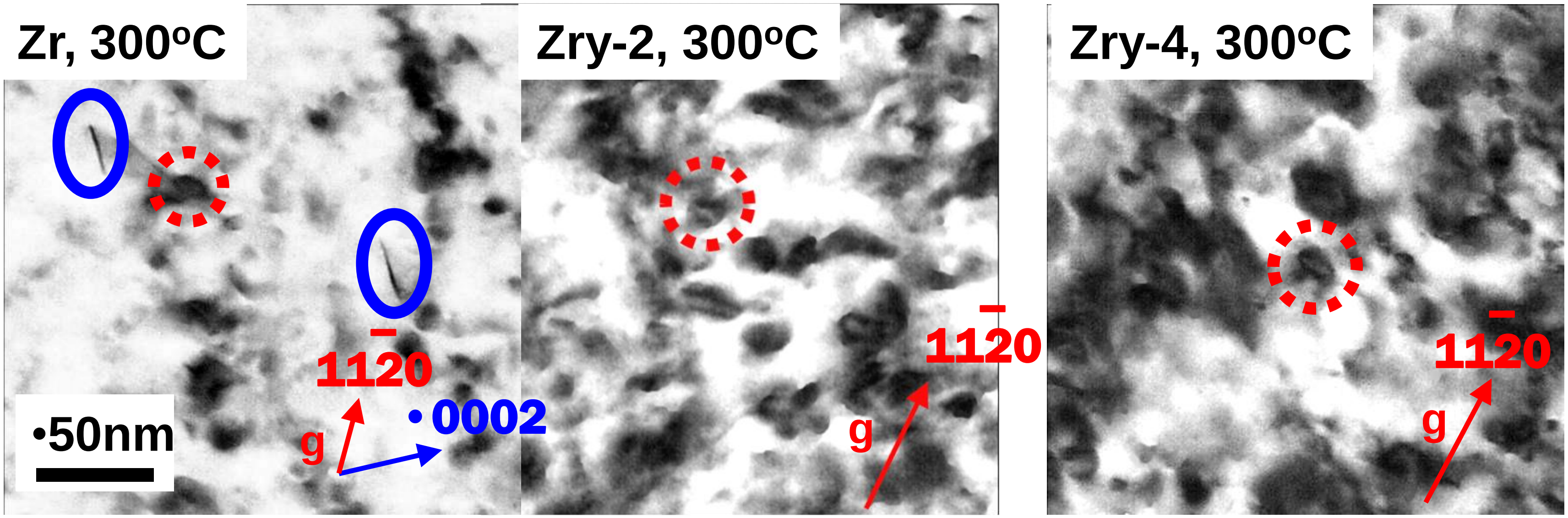
Results - Damage structure formed in Zry-2 at 300ºC



Dislocation loops (1.5 dpa)
Mean size: 17 nm
Number density: 7.3×10^{21} m^{-3}

Dislocation loops of a few nm in sizes were formed.
Number density of loops increased with increasing dose.

Results - Dislocation loops formed in Zr alloys (1.5dpa)



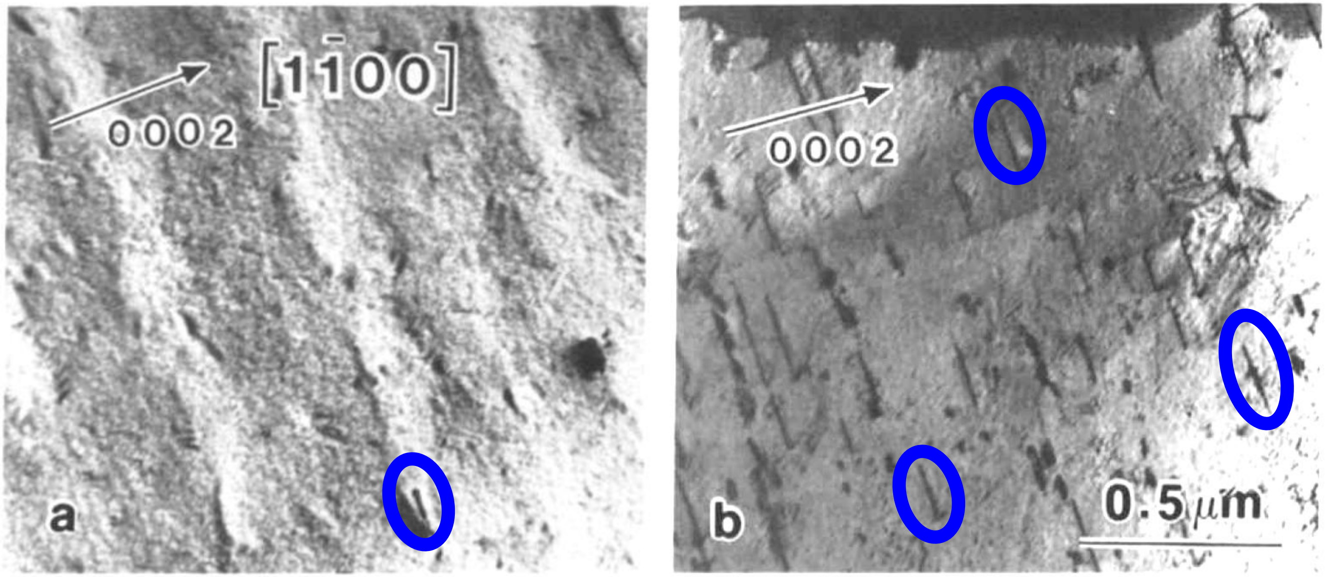
Line：<c> type   Circle：<a> type

Formation of the <c> type loops was observed on Zr.

Impurities in the matrix might affect for the formation of the <c> type loops.

Discussion - Effect of impurities in Zr

High purity **Low purity**



Comparison of the defect structures in (a) high purity and (b) low purity Zr, following irradiation at 700K to a fluence of 1.5×10^{26} n m^{-2} (~30 dpa) in EBR-II.

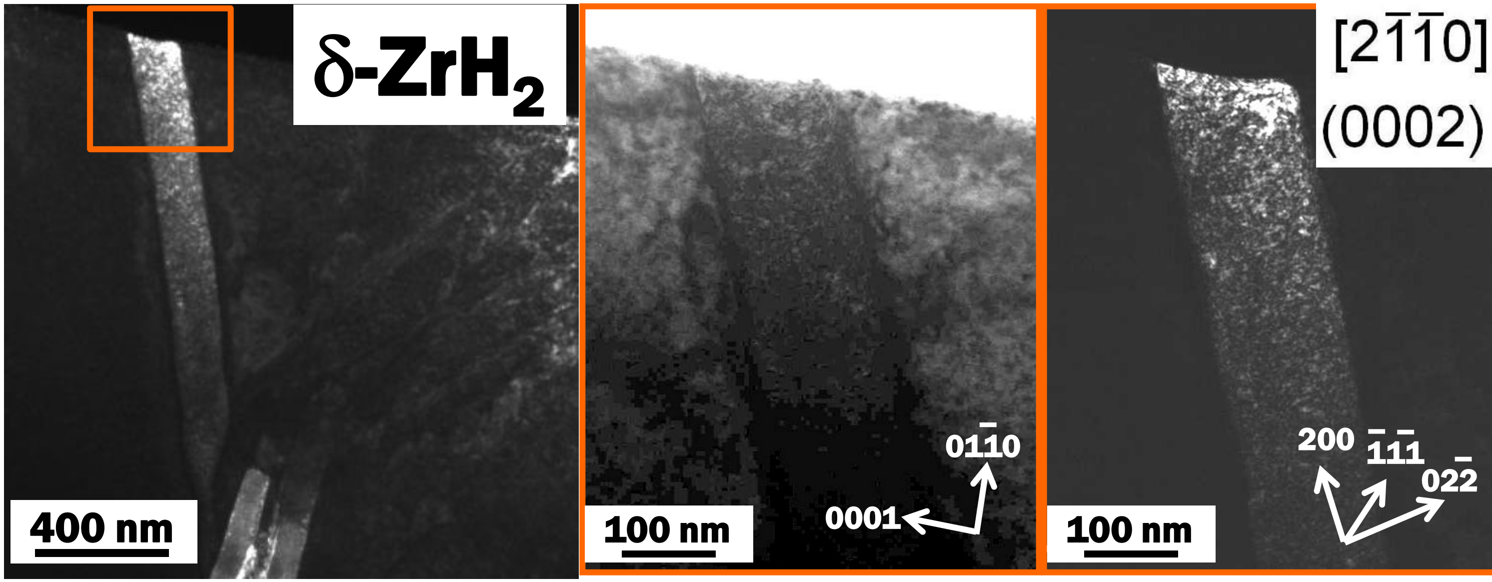
Ingot analyses for high purity and low purity Zr major impurities (ppm by weight)

	High purity	Low purity
C	60-70	130-180
Fe	200-260	640-760
O	150-350	970-990

High levels of impurities could affect for the formation of the <c> type loops.

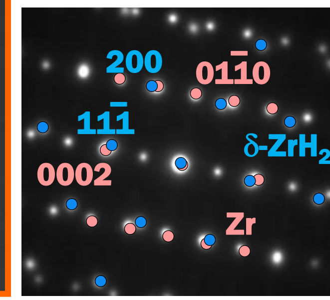
M. GRIFFITHS and R.W. GILBERT, J. Nucl. Mater. 150 (1987) 169-181

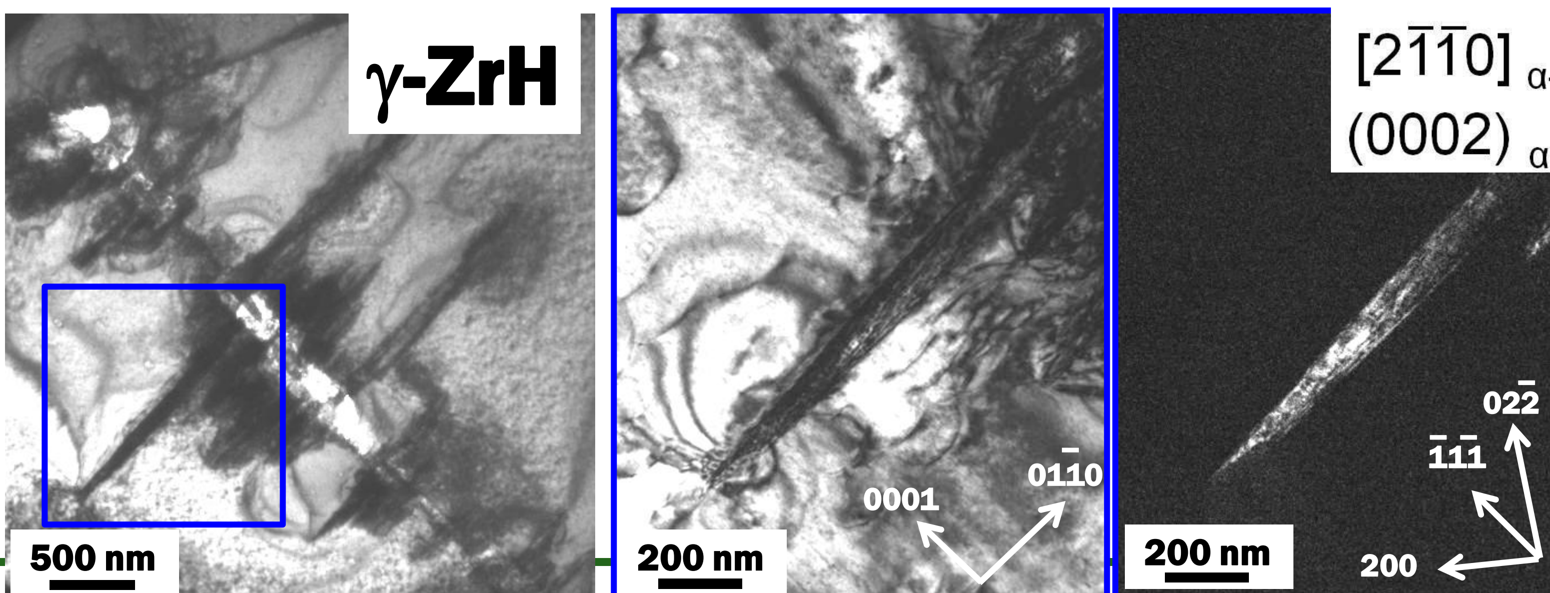
Two types of hydride precipitate in Zr



$[2\bar{1}\bar{1}0]_{\alpha\text{-}Zr} \, // \, [011]_{\delta\text{-}ZrH_2}$

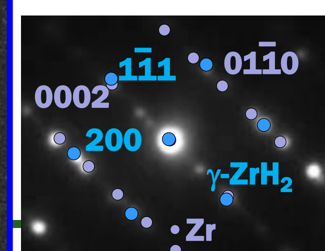
$(0002)_{\alpha\text{-}Zr} \, // \, (11\bar{1})_{\delta\text{-}ZrH_2}$





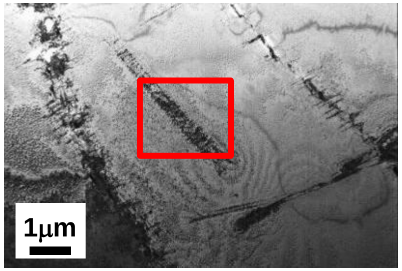
$[2\bar{1}\bar{1}0]_{\alpha\text{-}Zr} \, // \, [011]_{\gamma\text{-}ZrH}$

$(0002)_{\alpha\text{-}Zr} \, // \, (11\bar{1})_{\gamma\text{-}ZrH}$

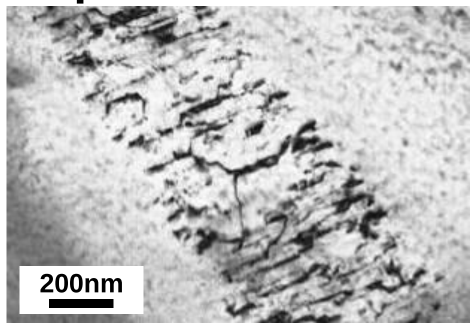


Irradiation behavior of δ-hydride at 300ºC

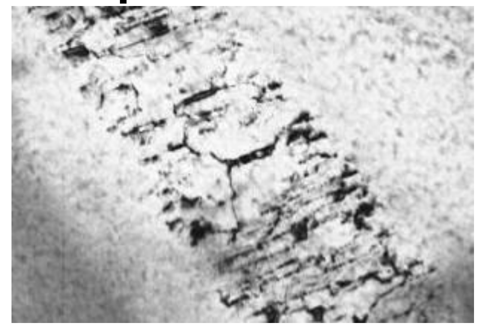
Low mag.



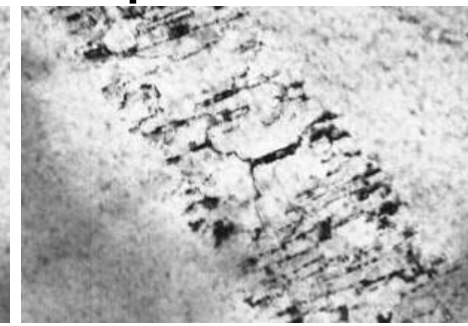
0 dpa



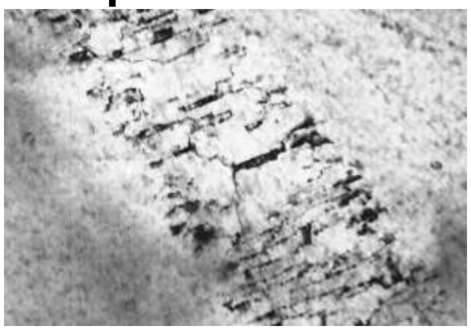
0.1 dpa



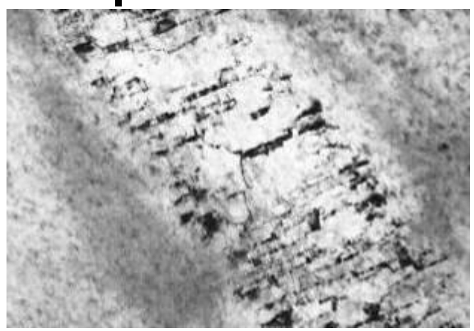
0.2 dpa



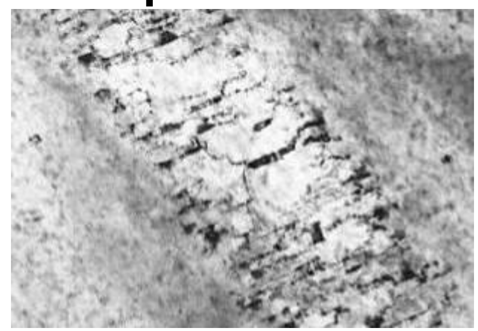
0.3 dpa



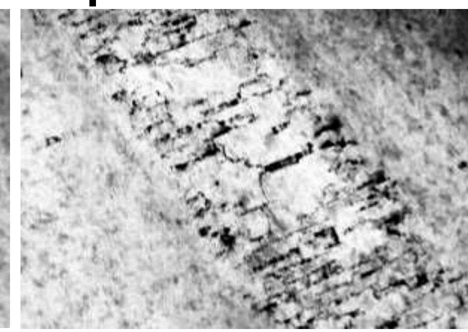
0.5 dpa



0.75 dpa

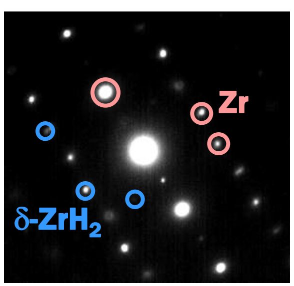


1 dpa

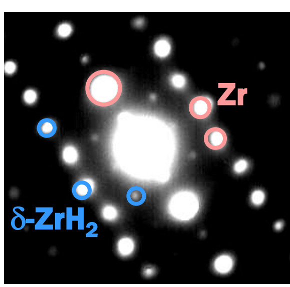


Width of the hydrides didn't change during electron irradiation.

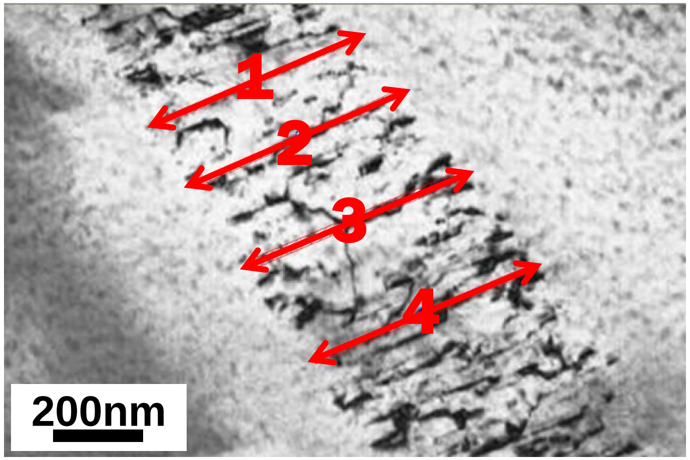
Before

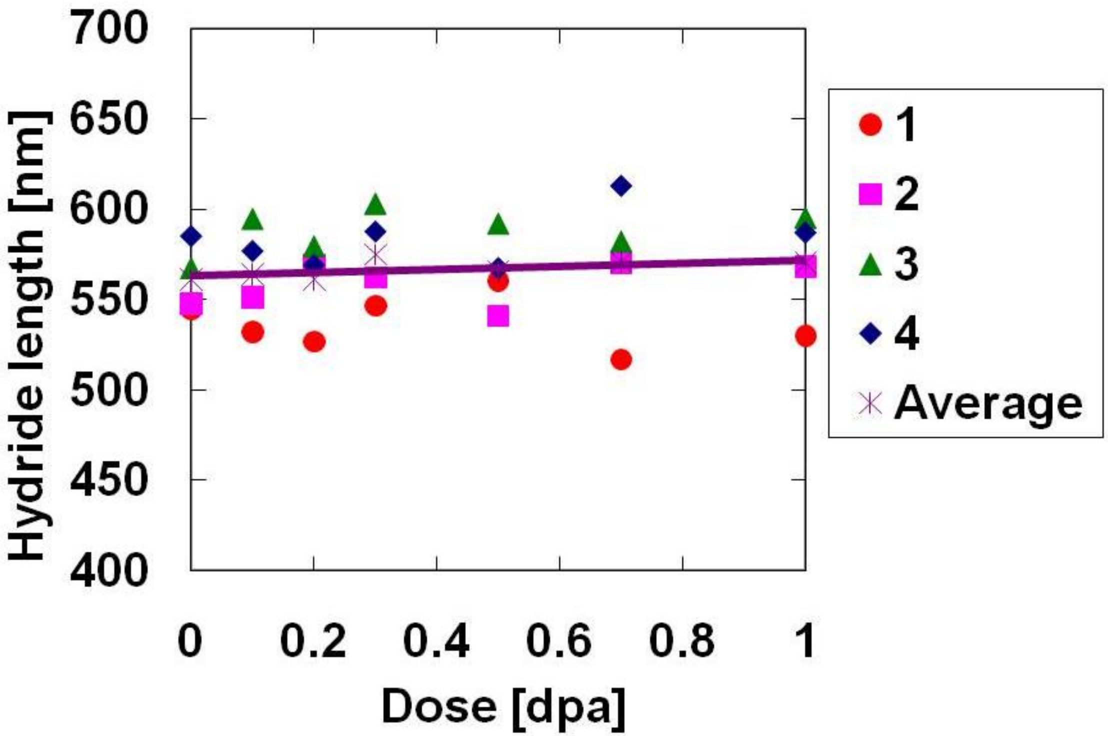


After



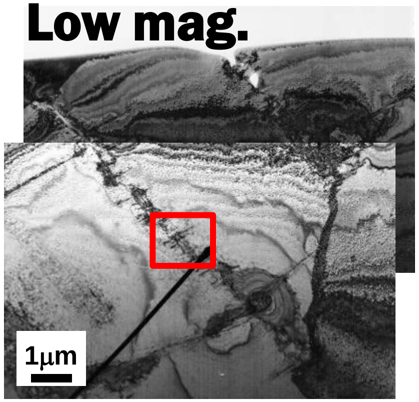
Irradiation behavior of δ-hydride at 300ºC



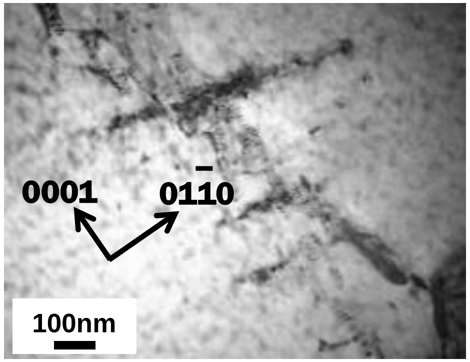


δ-hydrides were stable during electron irradiation.

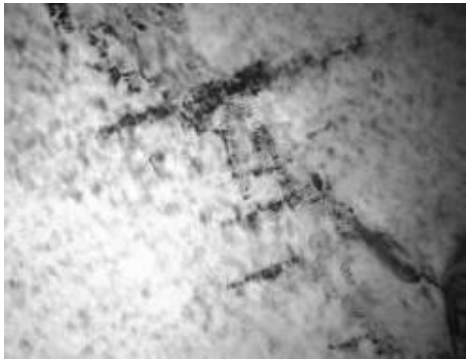
Irradiation behavior of γ-hydride at 300ºC



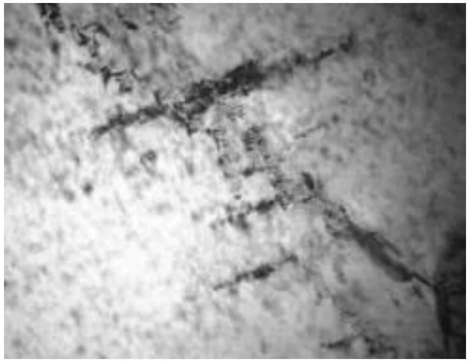
0 dpa



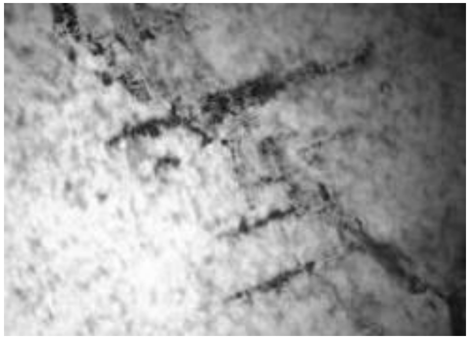
0.4 dpa



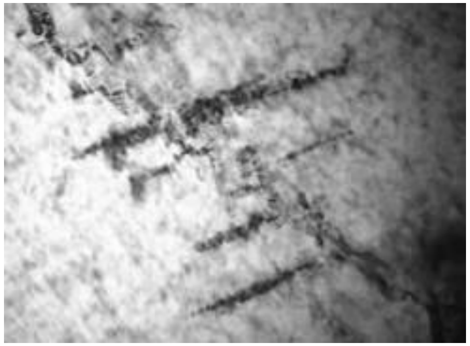
0.6 dpa



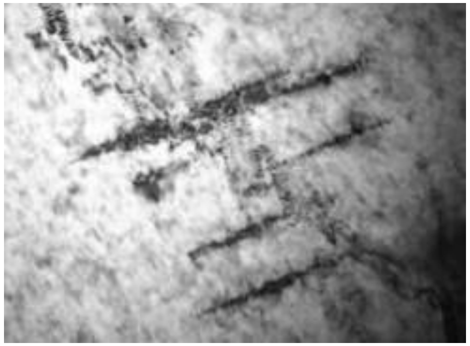
1 dpa



2 dpa



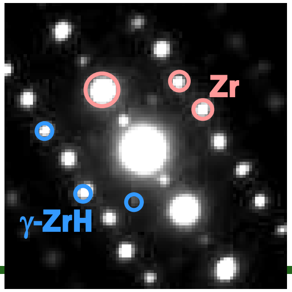
3 dpa



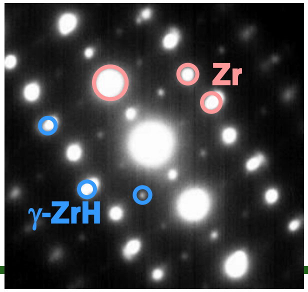
5 dpa

γ-hydrides grew to $[01\bar{1}0]$ orientation of Zr matrix.

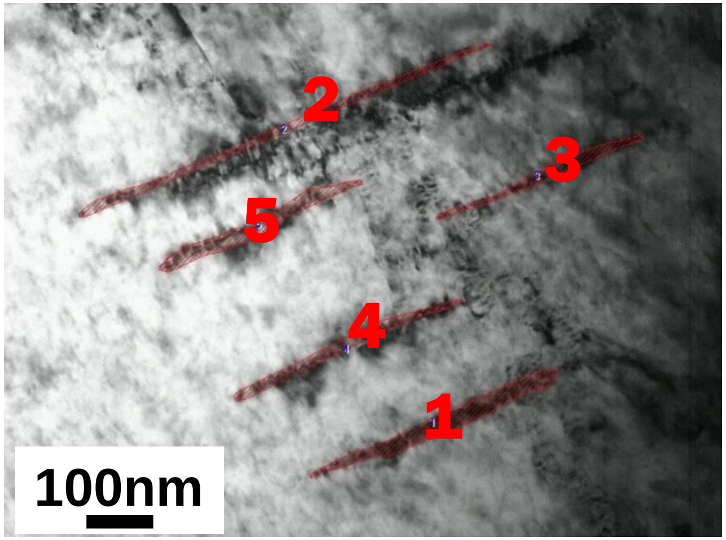
Before

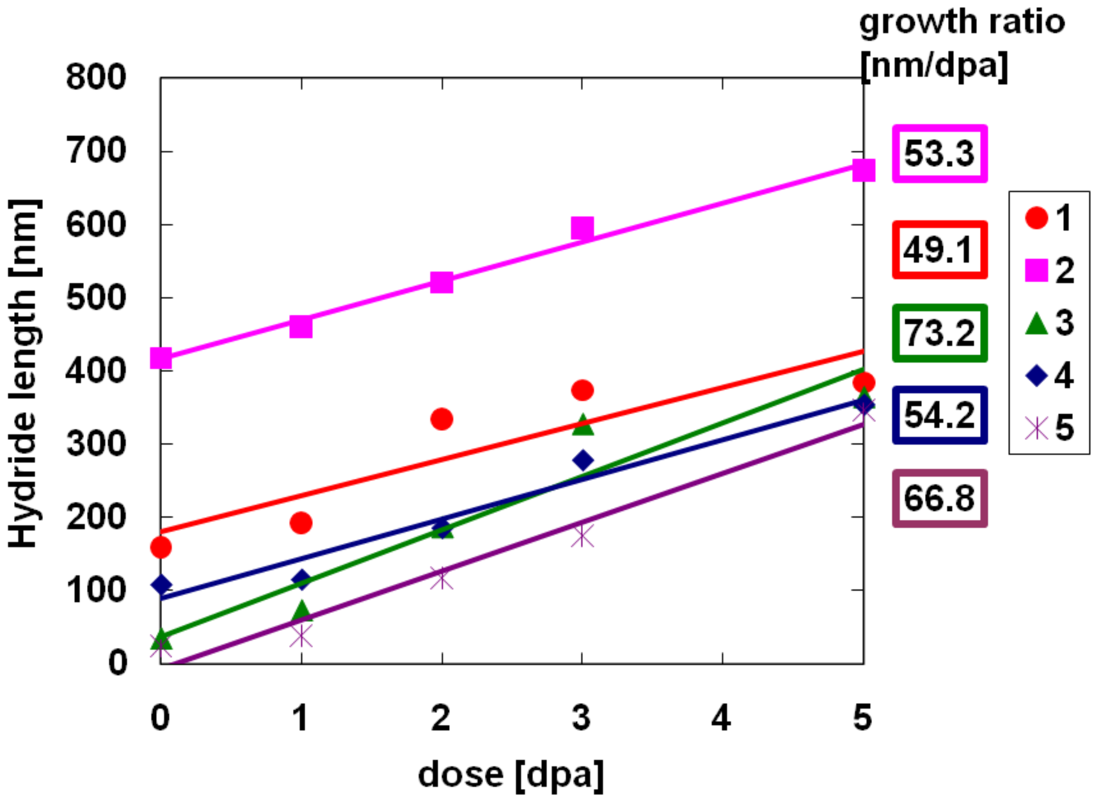


After



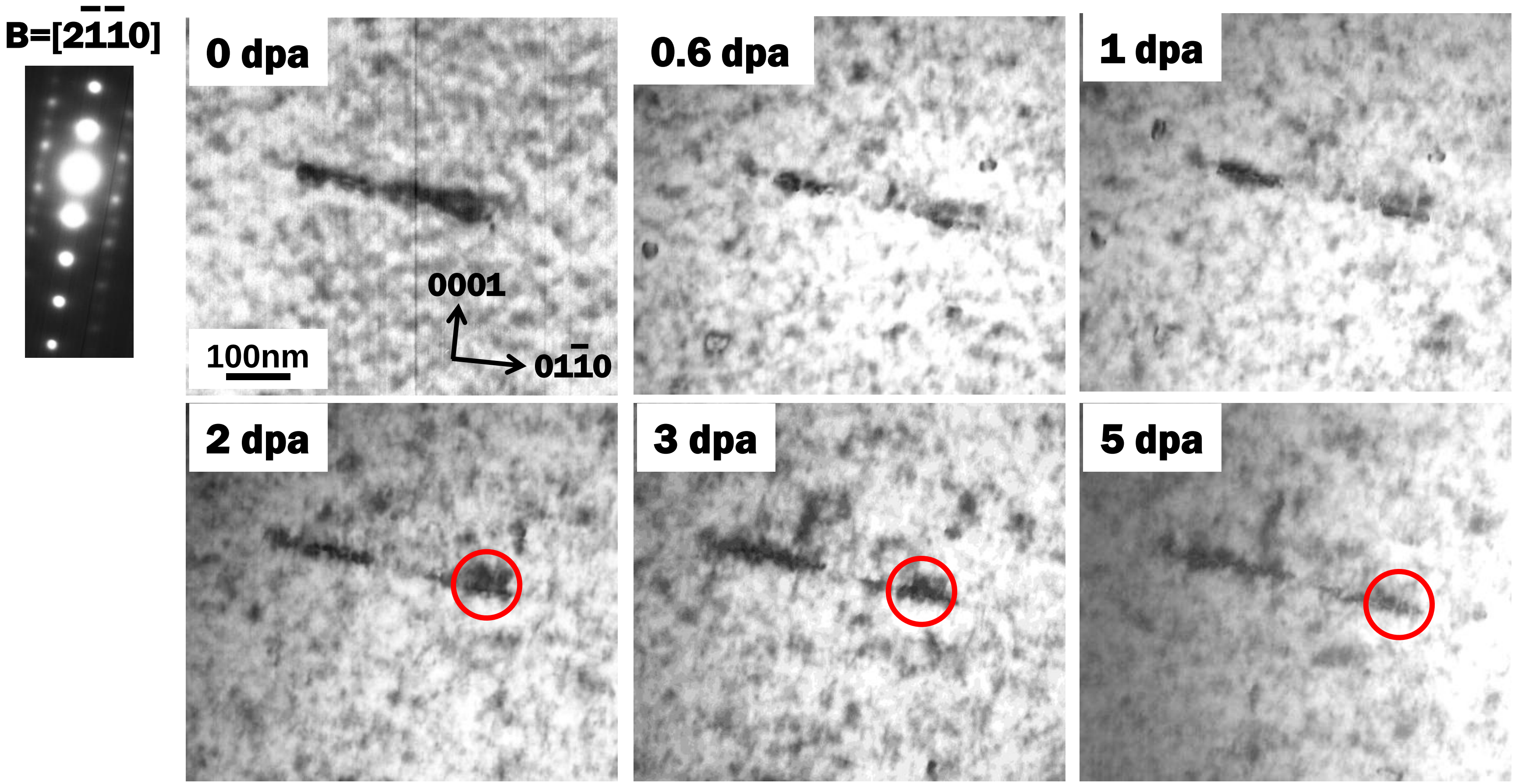
Irradiation behavior of γ-hydride at 300ºC





γ-hydrides showed linear growth during electron irradiation.

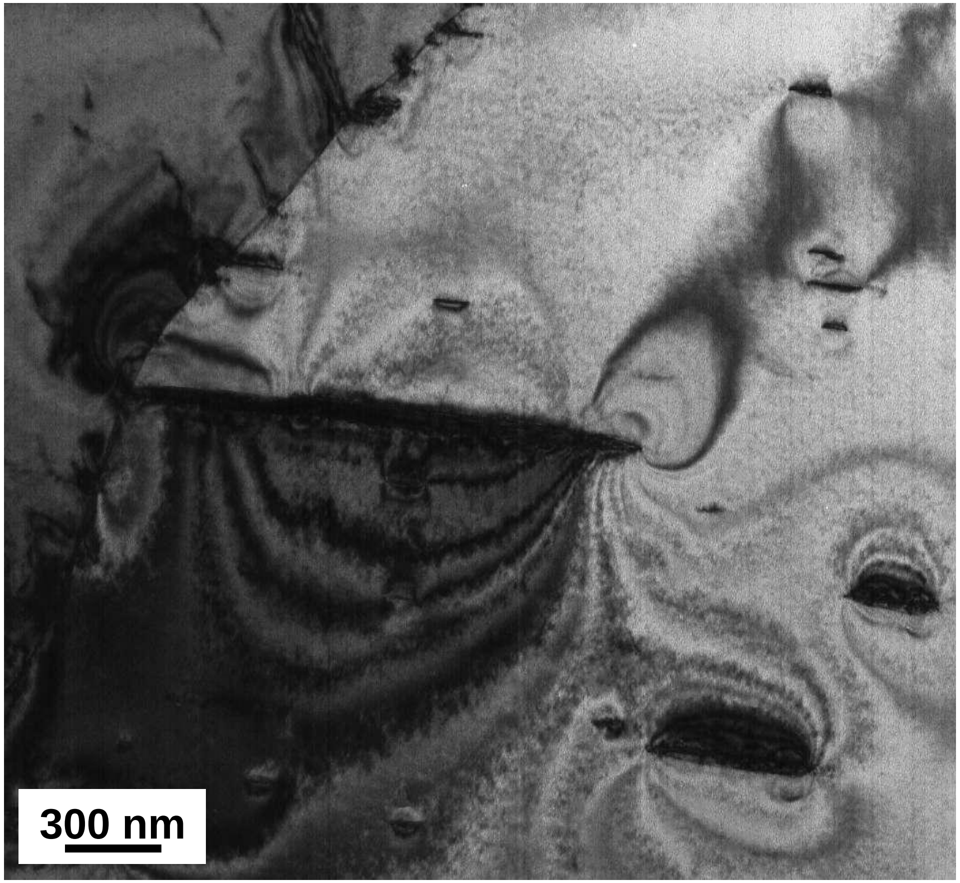
Dislocation loop nucleation close to the γ-hydride at 300ºC



<a> type dislocation loops were formed preferentially close to the hydride.

Discussion - Difference of the irradiation behavior

- ✓ γ-hydrides have strain fields.
- ✓ Self-interstitial atoms and/or hydrogen atoms induced by irradiation would move to hydride because of these strain fields.



γ-hydrides and associated strain fields.

These displacement atoms would be attracted by the hydride strain fields, leading to Hydride growth and loop nucleation close to the hydride.

Summary-1

Damage structures

- ✓ Most of the damage structures induced in Zr alloys by electron irradiation were <a> type dislocation loops (10~20 nm in size, and number density ≒ 10^{22} m^{-3}).
- ✓ As the difference of the samples, the <c> type loops were formed mainly in Zr, less in Zry-2 and -4, and impurities in the matrix could affect the formation of <c> type loops.

Irradiation behavior of hydride

- ✓ Plate like δ-hydrides were not changed, but Needle-like γ-hydrides grew during electron irradiation.
- ✓ <a> type dislocation loops were nucleated close to the γ-hydride during electron irradiation.
- ✓ Hydride growth and loop nucleation would be caused by the hydride strain fields.

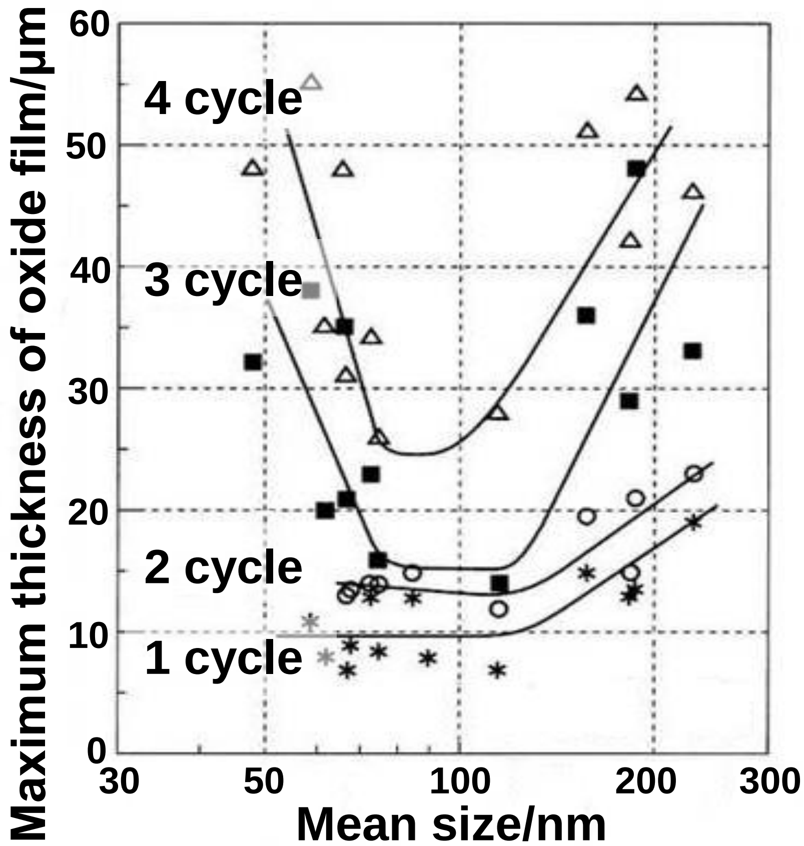
Introduction

Corrosion resistance depends on precipitates behavior

- size
- distribution

but…

Few works about stability of precipitates in Zr-Nb alloy under irradiation



Ref. ジルコニウム合金ハンドブック

Objective-2

Stability of precipitates in Zr-Nb alloy (Zr-1.0Nb-0.1Fe-1.0Sn) under irradiation

Experimental

Specimen (Zr-1.0Nb-0.1Fe-1.0Sn)

Preparation for TEM specimens
- punch-out of disks (3mm ϕ)
- electropolishing

Electron irradiation

Accelerating Voltage [kV]	1250
Temperature [^{o}C]	300, RT
Dose rate [dpa/s]	3×10^{-3} 2×10^{-3}
Maximum dose [dpa]	5, 10

Ni^{+} ion irradiation

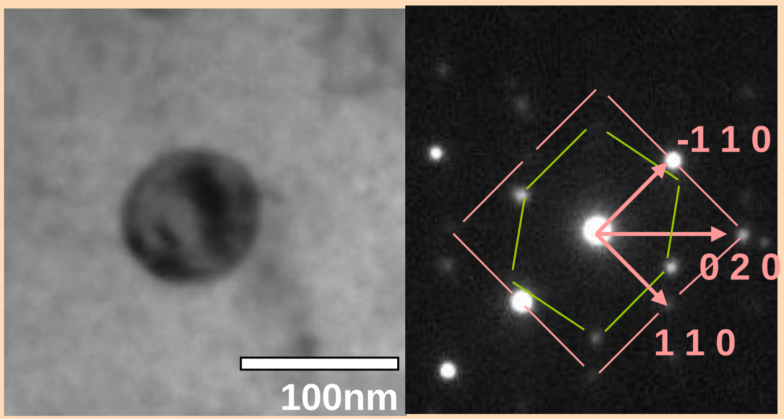
Accelerating Voltage [kV]	250
Temperature [^{o}C]	300
Dose rate [dpa/s]	6.3×10^{-3}
Maximum dose [dpa]	5

Preparation for TEM specimens
- punch-out of disks (3mm ϕ)
- electropolishing

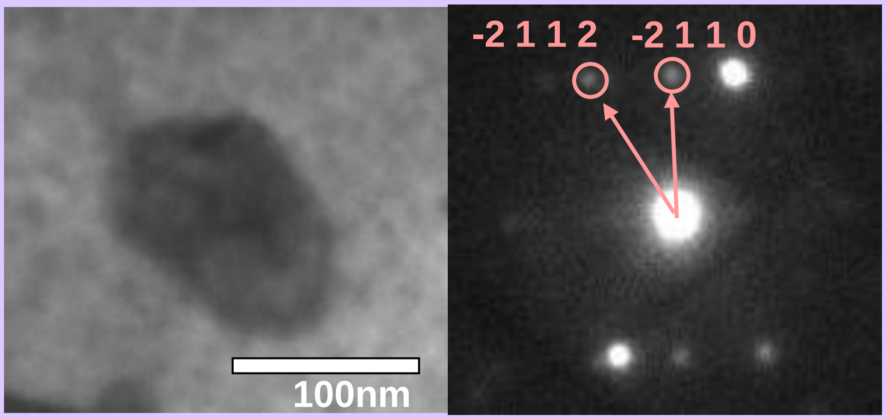
TEM observation, EDS

Character of precipitates

Zr-Nb type



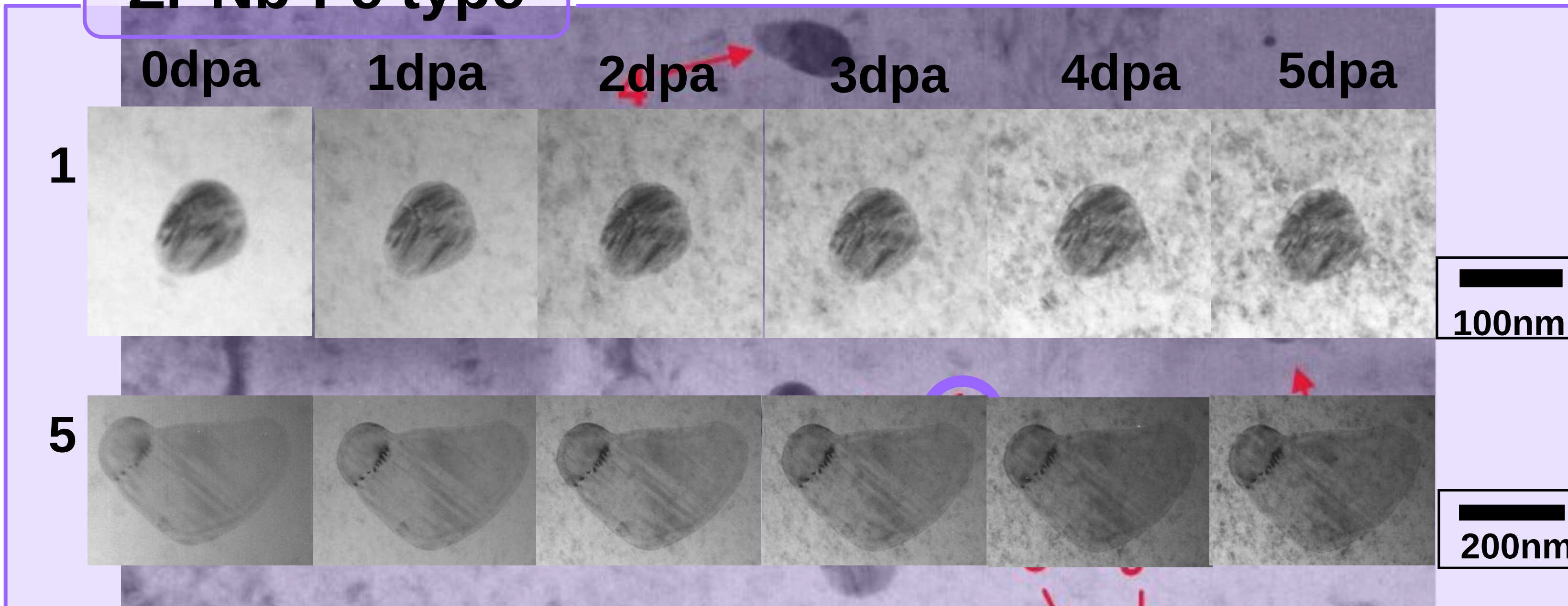
Zr-Nb-Fe type



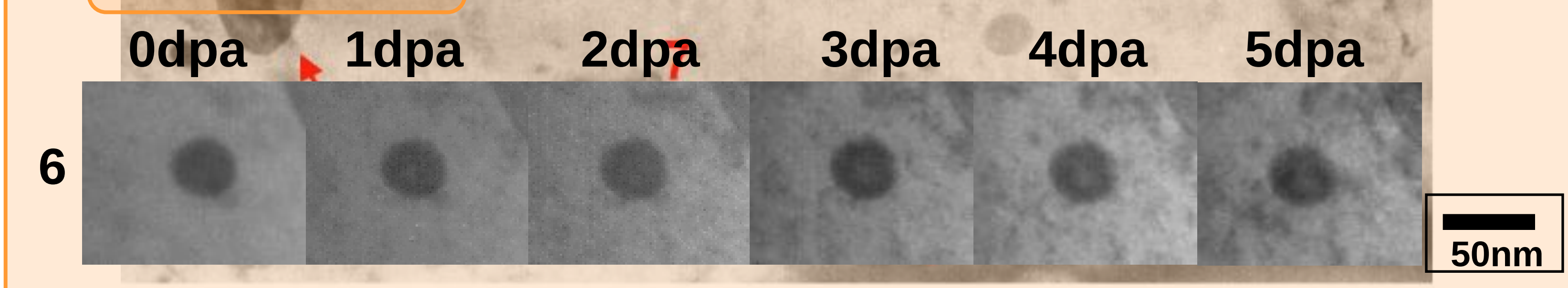
Type	Structure	Lattice parameter	Mean size	X_{Fe}≡Fe/(Nb + Fe)
Zr-Nb type	BCC β-Nb	a=3.3Å	40nm	
Zr-Nb-Fe type	HCP $Zr(Nb, Fe)_2$	a=5.3Å c=8.75Å	100nm	~0.28

In-situ Electron irradiation experiment at 300℃

Zr-Nb-Fe type



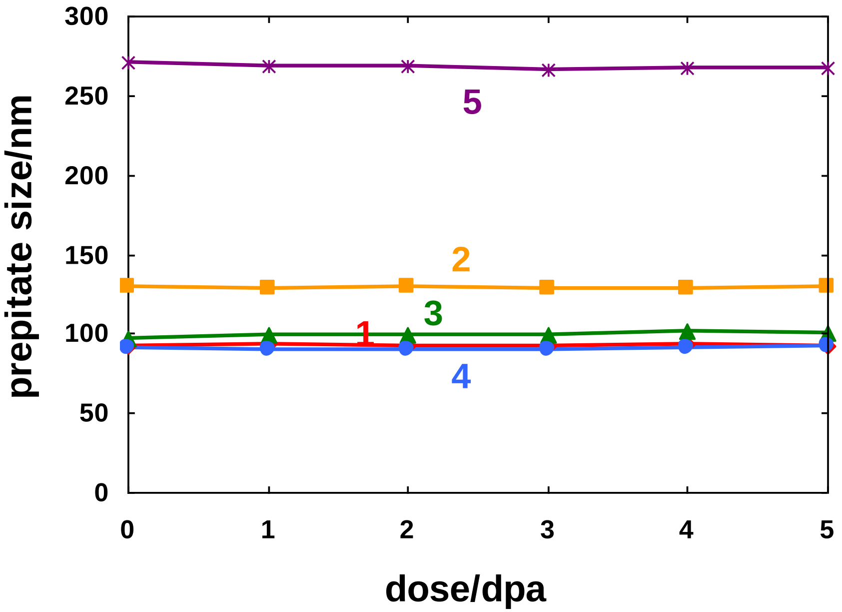
Zr-Nb type



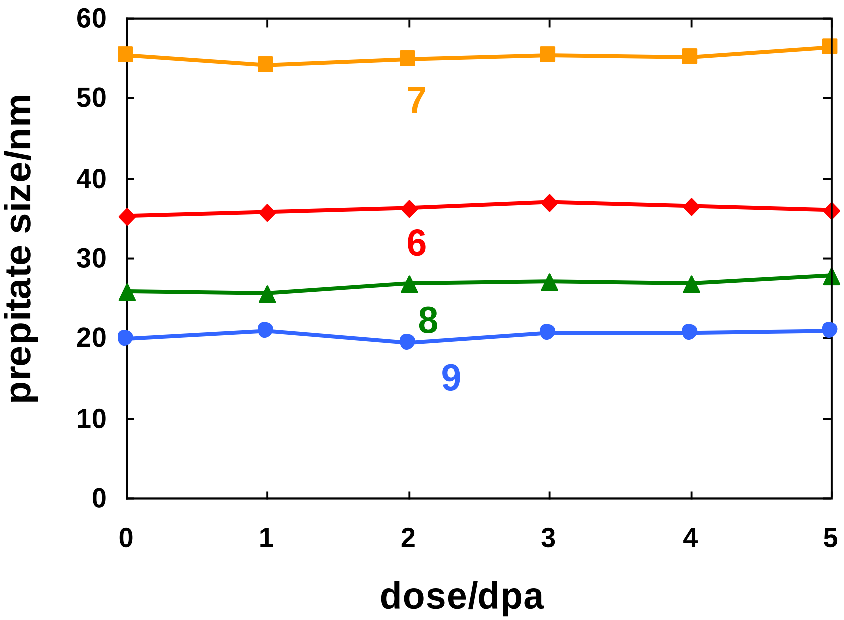
Result & discussion

In-situ Electron irradiation experiment at 300℃

Precipitates ♯1 - 5

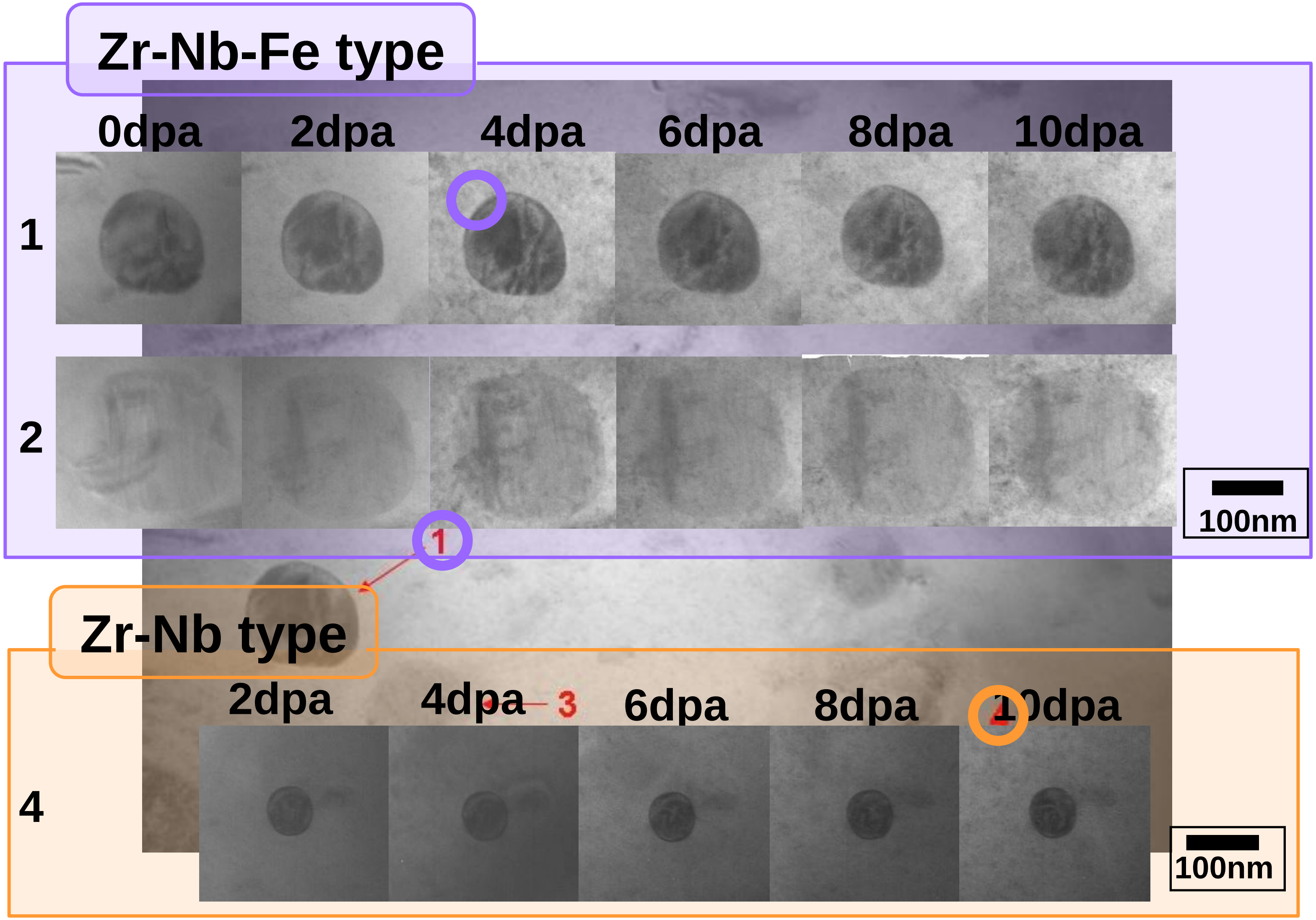


Precipitates ♯6 - 9



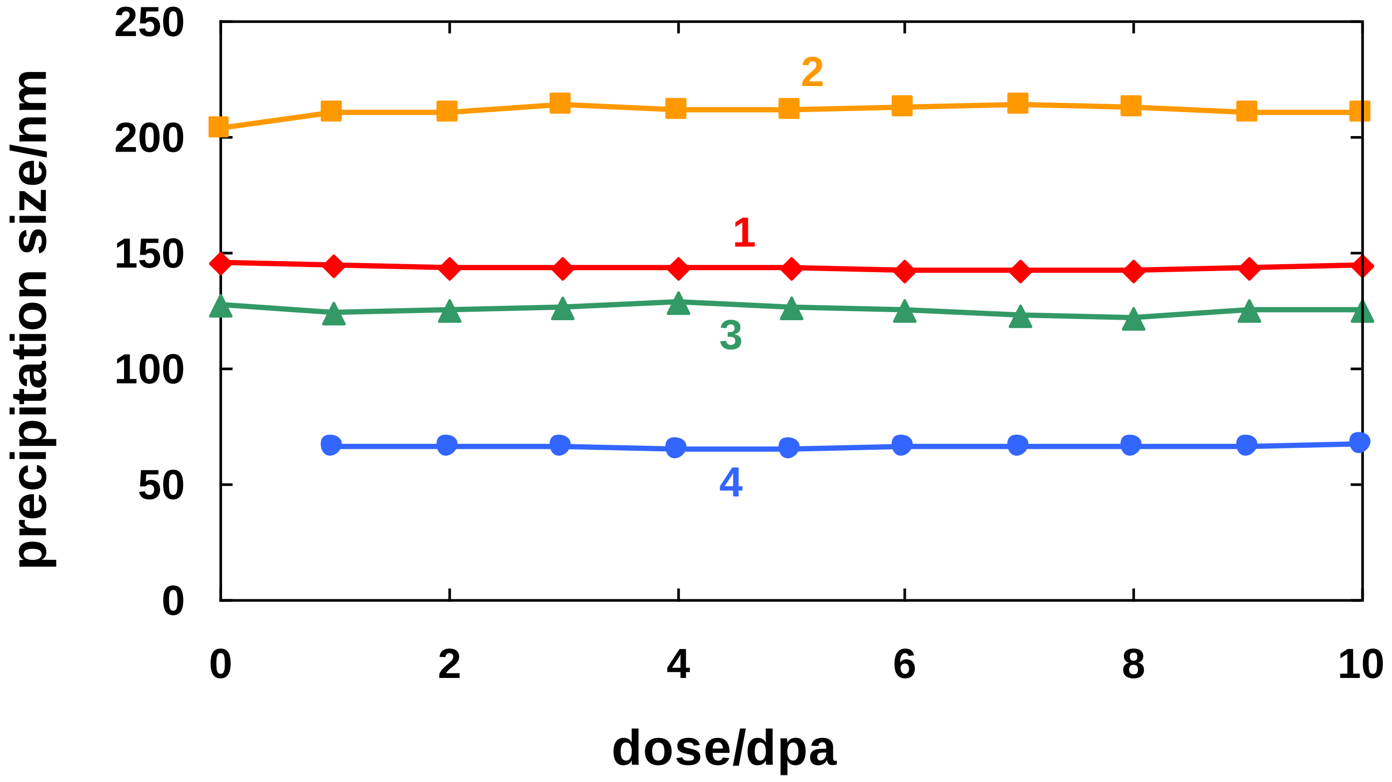
Size of precipitates did not change under electron irradiation at 300℃.

In-situ Electron irradiation experiment at RT



Result & discussion

In-situ Electron irradiation experiment at RT

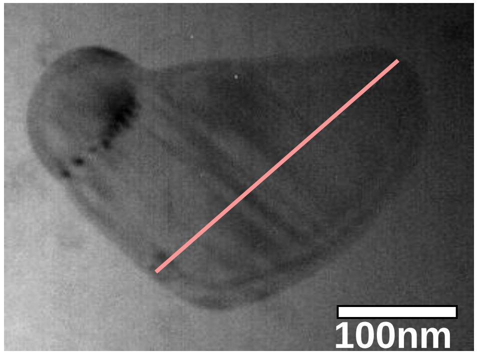


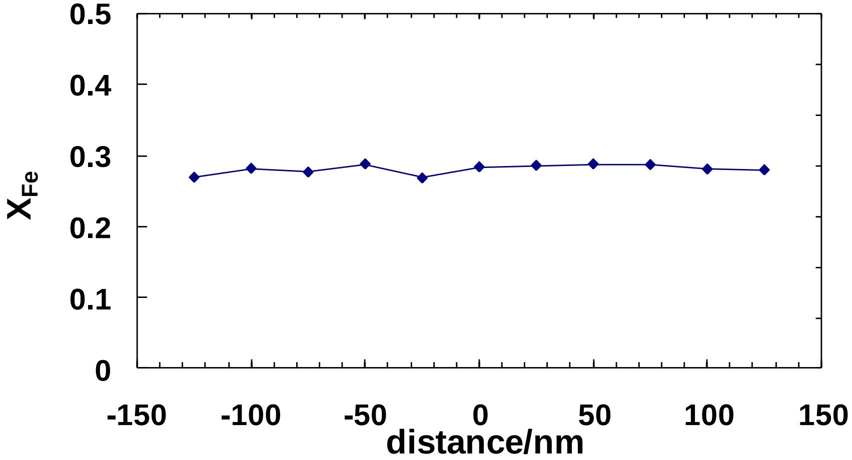
Size of precipitates did not change under electron irradiation at RT.

Result & discussion

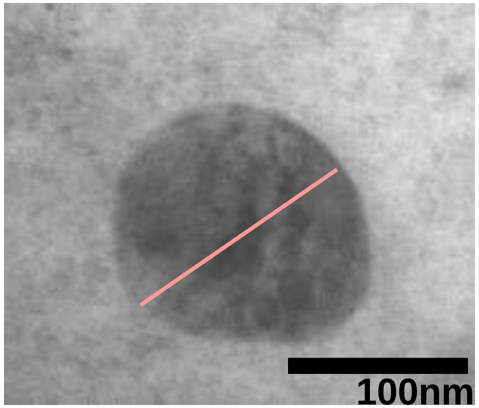
After electron irradiation

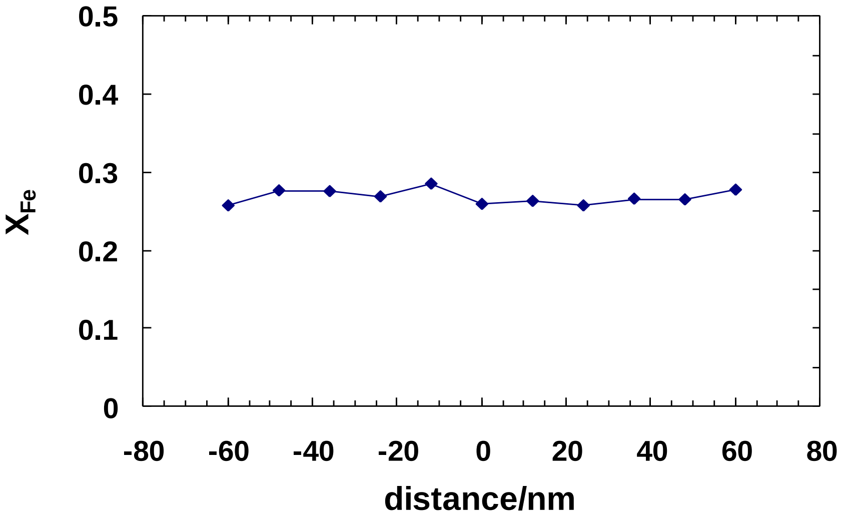
at 300℃
Precipitate #5





at RT
Precipitate #1



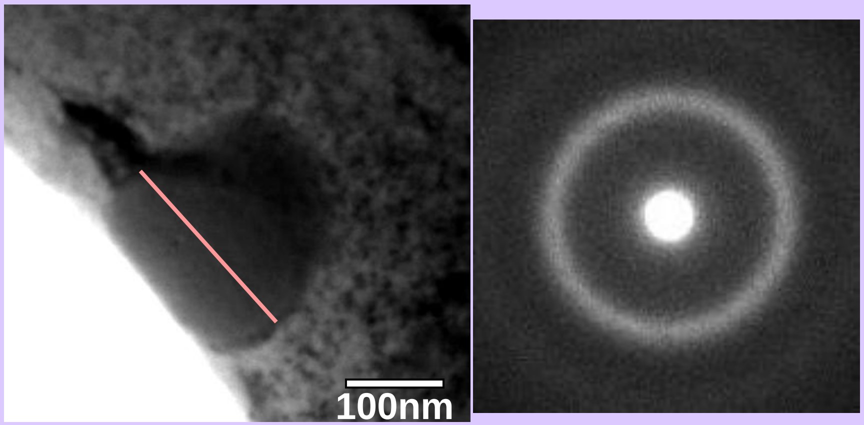


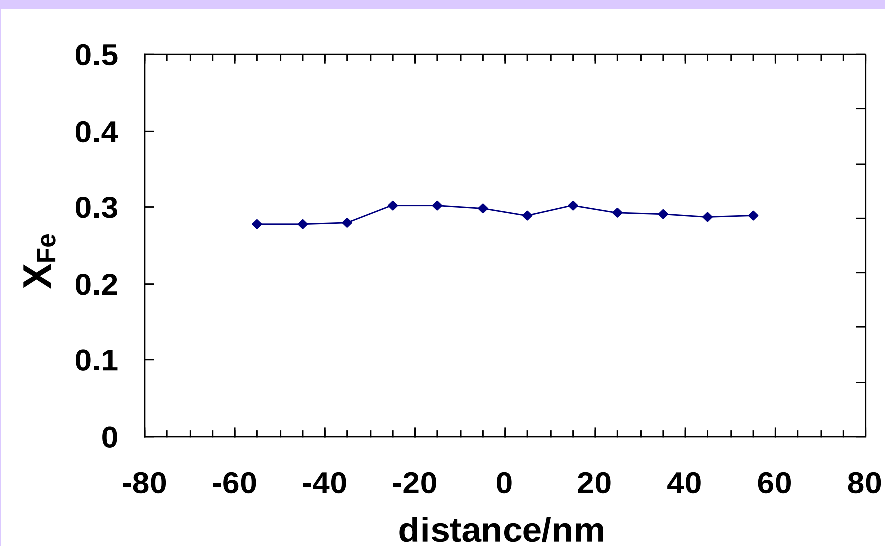
X_{Fe} did not change after electron irradiation.

Result & discussion

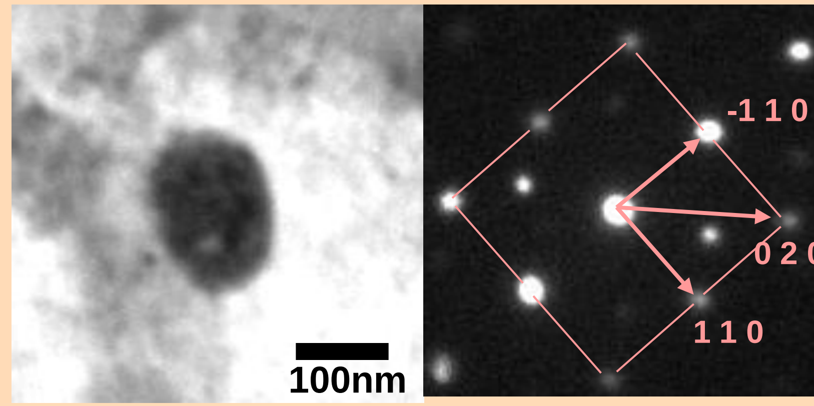
Ni$^+$ ion irradiation up to 5dpa at 300℃

Zr-Nb-Fe type





Zr-Nb type



- **Amorphization of Zr-Nb-Fe type precipitates were observed.**
- **Zr-Nb type precipitates would be stable in this condition.**

Summary-2

✓ There is a difference in damage morphology between electron and ion irradiation. Stability of precipitate was affected by the type of irradiation damage, such as PKA and cascade.

Electron irradiation

✓ Precipitates were stable after electron irradiation up to 5 dpa at 300℃.

✓ Precipitates were stable after electron irradiation up to 10 dpa at RT.

Ni^+ ion irradiation

✓ Zr-Nb type precipitates were stable after Ni^+ ion irradiation up to 5 dpa at 300℃.

✓ Amorphization of Zr-Nb-Fe type precipitates were observed after Ni^+ ion irradiation up to 5 dpa at 300℃.