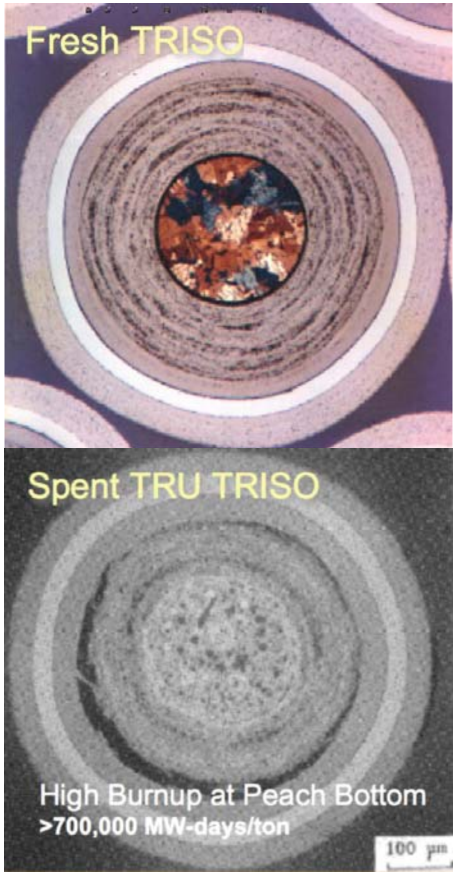

Radiation Stability of Ceramics for Advanced Fuel Applications

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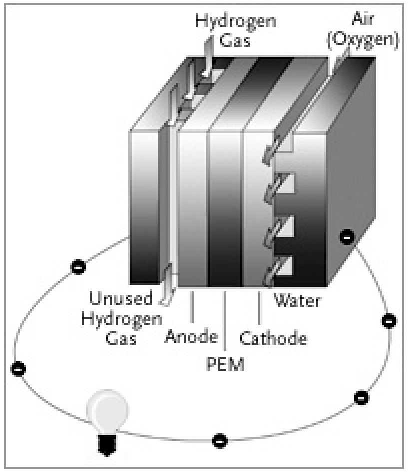
Engineering Physics Department
University of Wisconsin-Madison

Advanced Fuels

Advanced Fuels

Reduce High-level Waste Volume

Improve Thermal Efficiency and Produce High Temperature Process Heat



H Fuel Cell

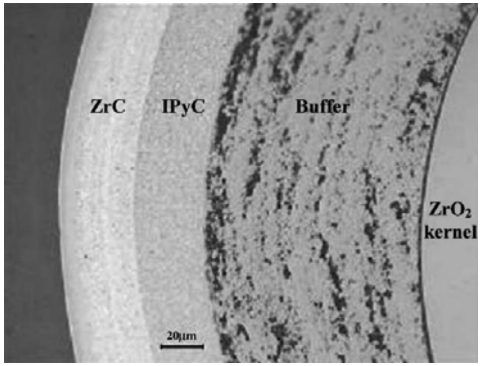
Materials Selection

Gas Cooled Fast Reactor Constraints	
Condition	Value
Melting temperature	>2000°C
Radiation resiliency	<2% Swelling over life time
Toughness	>12 MPa $m^{1/2}$
Thermal conductivity	>10W/m/K
Neutronic	Low σ_a

ZrN
ZrC
TiC
TiN
SiC

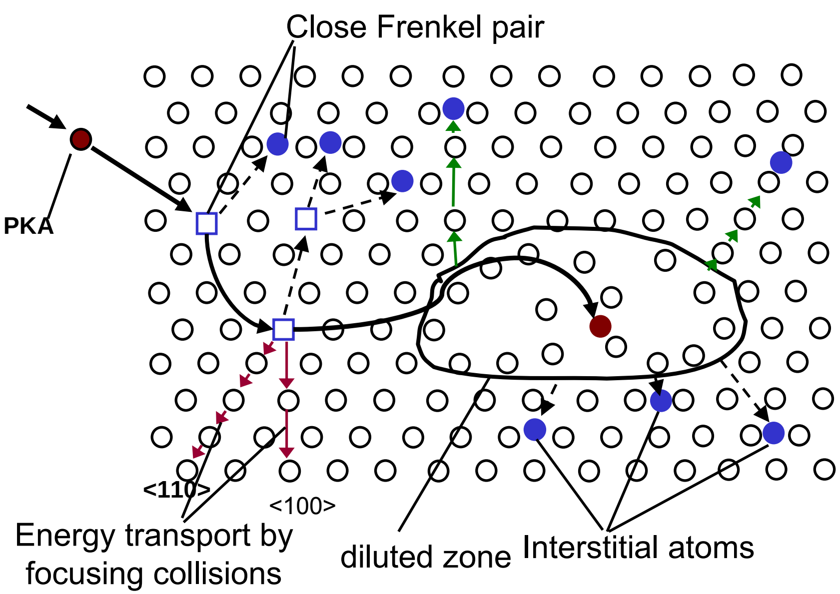
Candidates

- Applications
  - Matrix materials for dispersion fuel
  - Coating materials for particle Fuel
  - Fission products diffusion barrier coating layer (ZrC) for TRISO Fuel



Radiation Damage and Effects

- Microstructural evolution
  - Amorphization
  - Dislocation loops and networks
  - Voids
  - Microchemical changes (segregation and precipitates)
- Changes in properties
  - Hardening and embrittlement
  - Vulnerability to corrosion
  - Reduction of thermal conductivity



ATR-PIE project

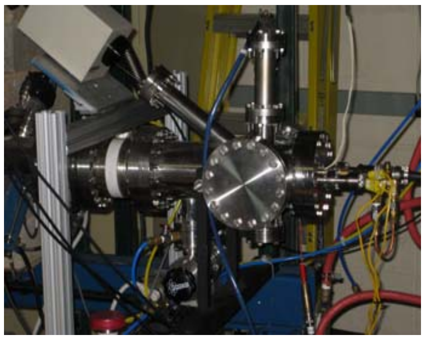
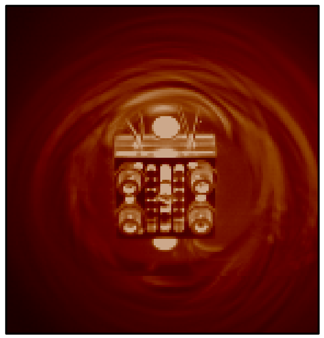
- **Objectives:**
  - Provide the microstructural data of the GFR candidate ceramics under neutron irradiation
  - Validate the using ion irradiation to understand the radiation effects from energetic neutrons in refractory ceramics
- **Materials:**
  - ZrC, TiC, ZrN and TiN irradiated to 1 dpa at 800 ºC
- **Approaches:**
  - TEM microstructural examination
  - Microhardness test

Synergy with Other DOE Funded Projects

- **NERI (Radiation-Stability of Candidate Materials for Advanced Fuel Cycles)**
  - Determine and understand the radiation stability of advanced fuel candidate materials in response to proton irradiation at temperatures between 600-900°C
- **Deep-Burn (Development of Transuranic Fuel for High-Temperature Helium-Cooled Reactors)**
  - Study the radiation response of ZrC at 1100-1400 ºC
  - Transport of silver fission product in ZrC

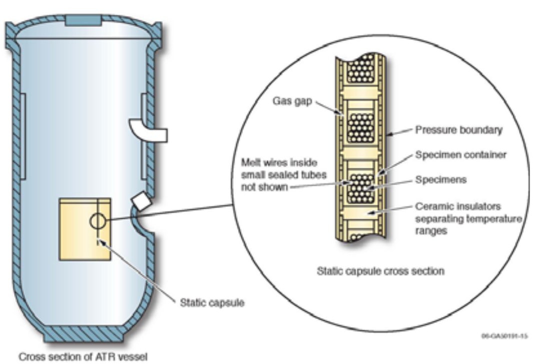
Approaches

Proton irradiation (T: 600, 800, 900, 1100 and 1400 ºC; and Dose: 0.35-3 dpa)

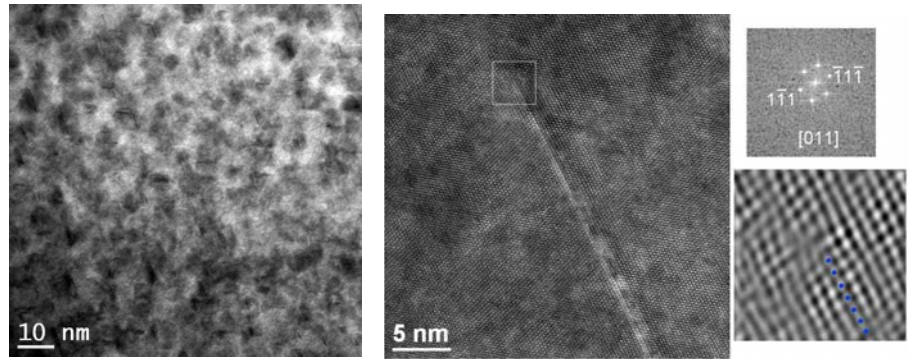
Beam terminal (UW Tandem Accelerator)

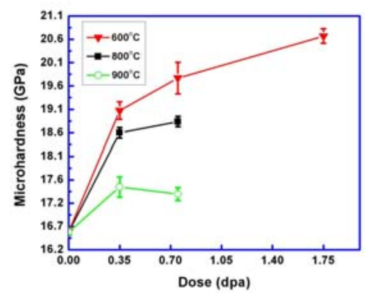
Neutron irradiation (T: 800ºC; and Dose: 1 dpa)



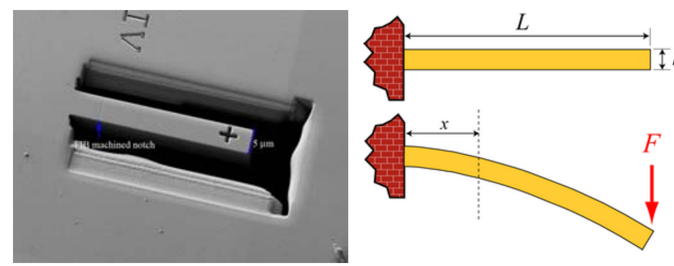
Ceramics irradiated in a static capsule in ATR, INL

Irradiated microstructure characterization (TEM, HR-TEM/STEM)

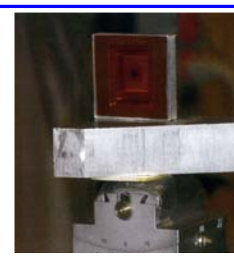




Vickers Test



Micro Fracture Test



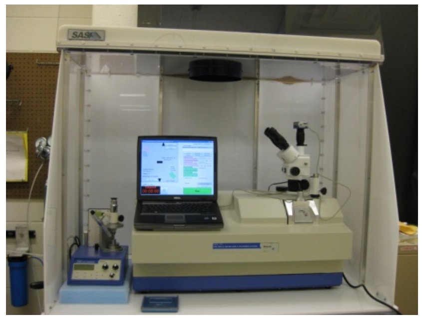
Microstructure and microchemical changes studied using APS (J. Terry)

- **X-ray diffraction**
- **Extended X-Ray Absorption Fine Structure (EXAFS)**

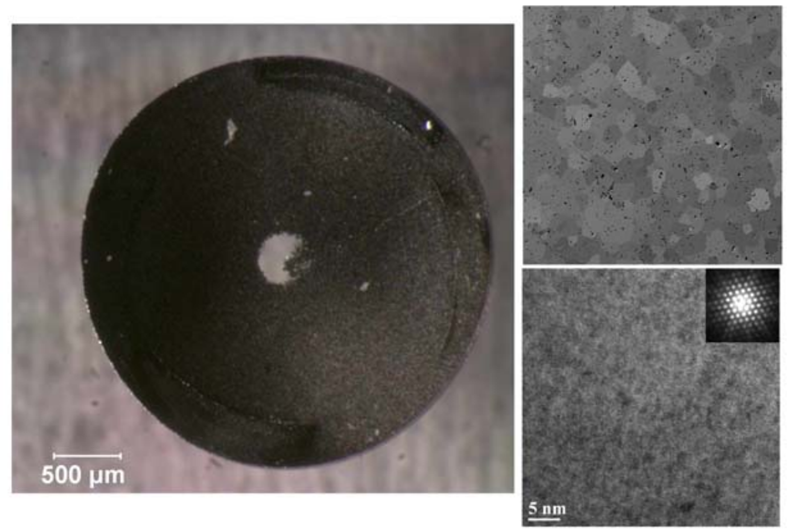
Sample sealed in a triple-contained cell

Post Irradiation Experiments (PIE): Characterization at U. Wisconsin

Univ. Wisconsin - Characterization Lab for Irradiated Materials (CLIM)



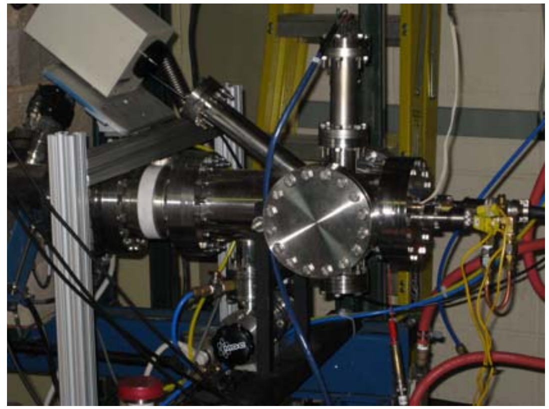
TEM sample preparation: electro-polisher, dimpler and ion mill in HEAP fume hood

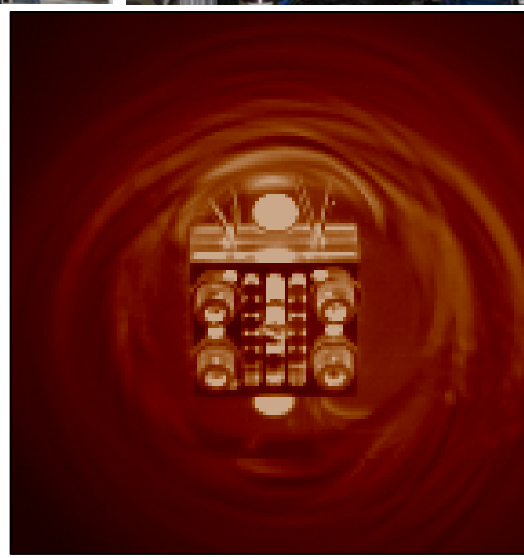


ZrC TEM specimen prepared by dimpling and ion milling method

Electron Microscopes: JEOL 200CX, JEOL 6610 SEM

Proton Irradiation Experimental





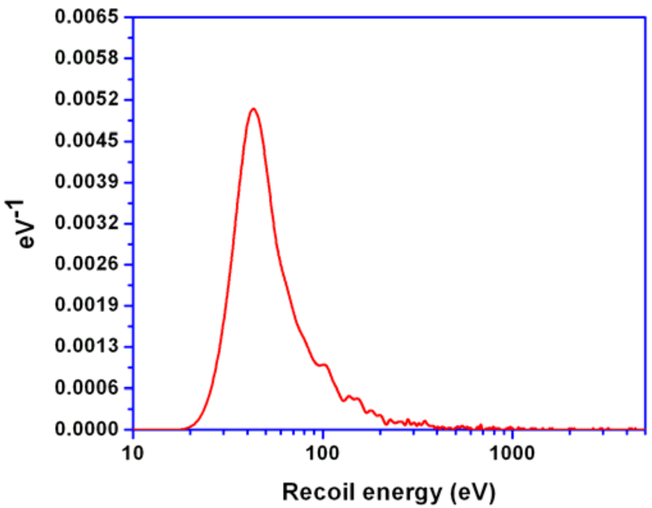
UW Tandem Accelerator Facility

- Energy: 1.7 MV with capability of accelerating protons to 3.4 MeV
- High Temperature: 600–1400 ºC (Sample temperature)
- RF source and SNICS source (Source of Negative Ions by Cesium Sputtering)

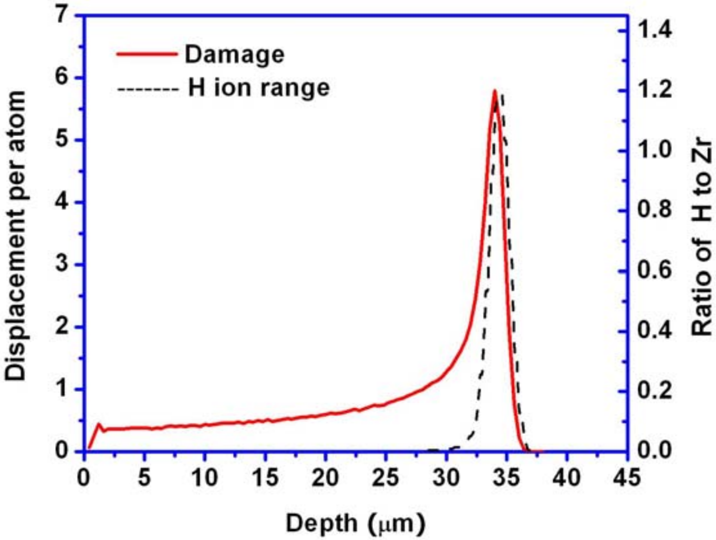
Real time monitoring of sample temperature and dose

- Three thermocouples
- Mikron Model 7302 infrared camera
- Quadra beam aperture

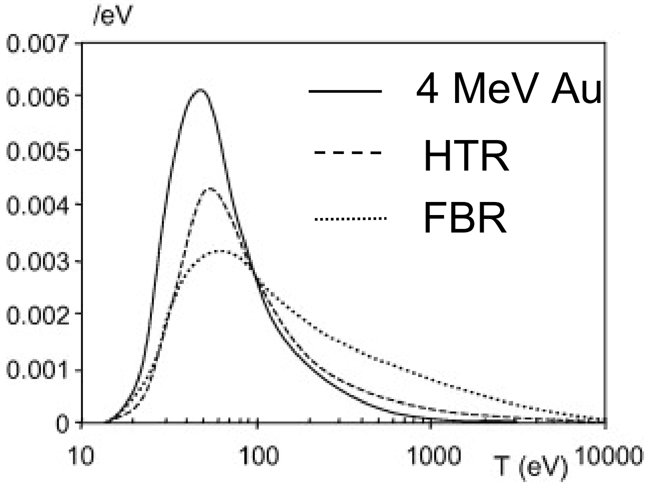
SRIM calculation



The primary knock-on atom spectrum of ZrC irradiated with 2.6 MeV protons as estimated from SRIM-2008



SRIM estimation of damage in ZrC irradiated with $1x10^{19}/cm^2$ 2.6MeV protons



Probability density of PKAs in ZrC irradiated in different conditions [Courtesy to D. Gosset]

Proton Irradiation Conditions

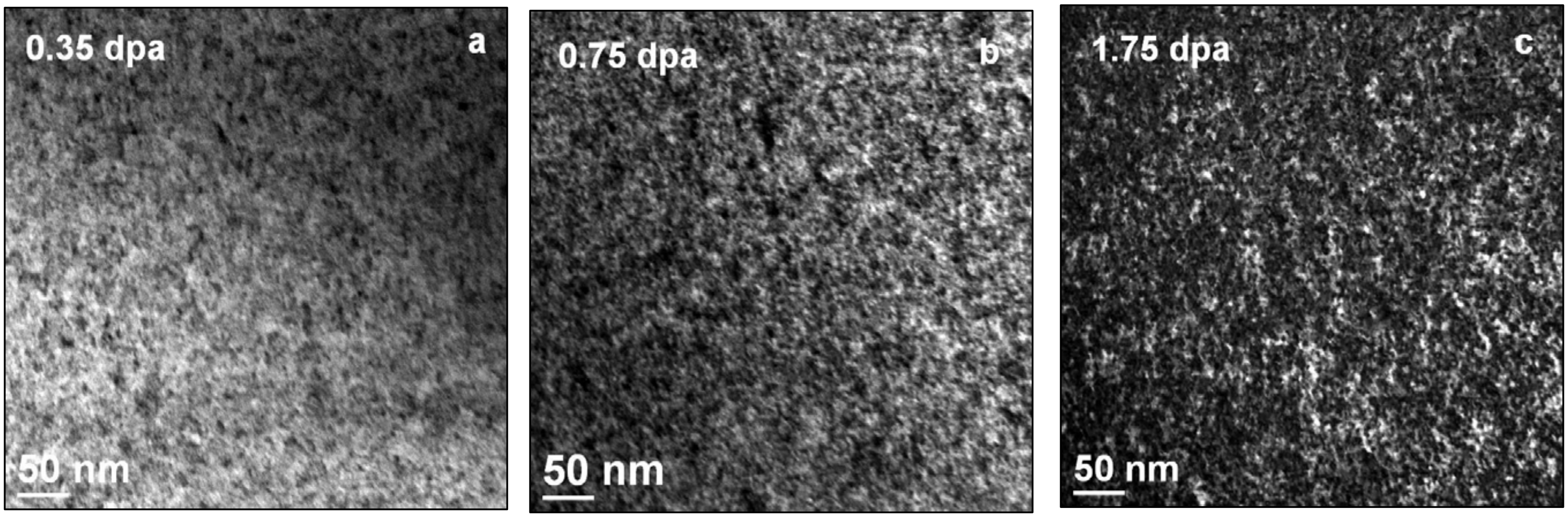
Beam Energy	2.6 MeV			
Materials	CERCOM (Stoichiometry: C/Zr= 1.01)			Zone-refined *
Temp (ºC)	600	800	900	1125
Dose (dpa)	0.35, 0.75 and 1.75			1 and 2

* Zone-refined ZrC (Applied Physic Technologies, Inc. McMinnville, Oregon)

Item	Target Composition	Measured C/Zr
1	$ZrC_{08\pm0.5}$	0.84
2	$ZrC_{09\pm0.5}$	0.89
3	$ZrC_{1.0\pm0.5}$	0.95
4	$ZrC_{1.1\pm0.5}$	1.05
5	$ZrC_{1.2\pm0.5}$	1.17

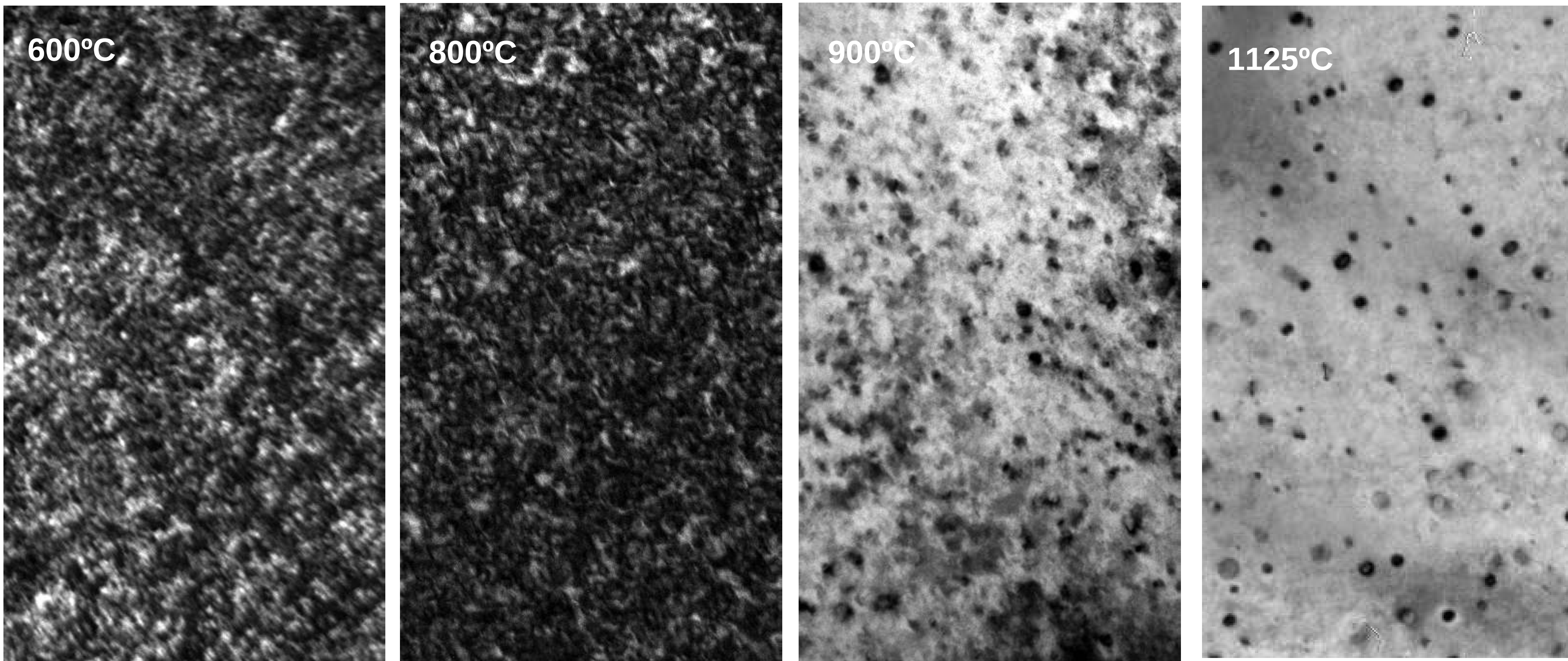
Dose effect — ZrC irradiated at 600 ºC

Bright Field Images g=200 near <011> zone axis



Highly strained field →

Temperature effect



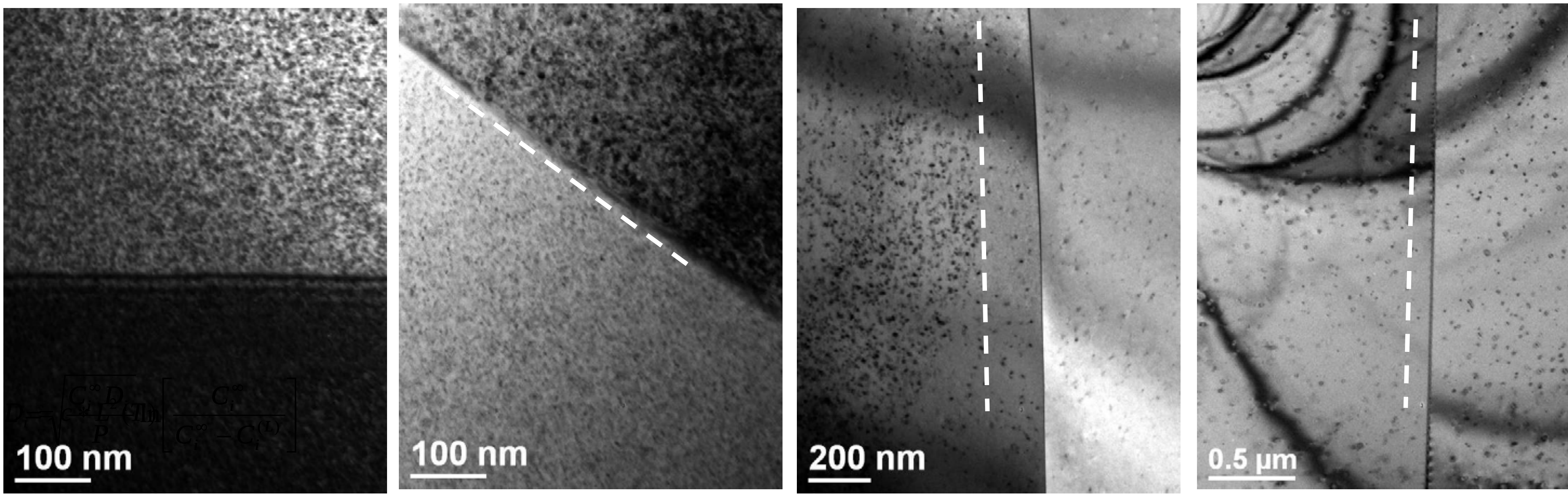
Faulted loops *b=a/3[111]*

Perfect loops *b=a/2[110]*

Size of dislocation loops →

← **Loop density**

Temperature effects

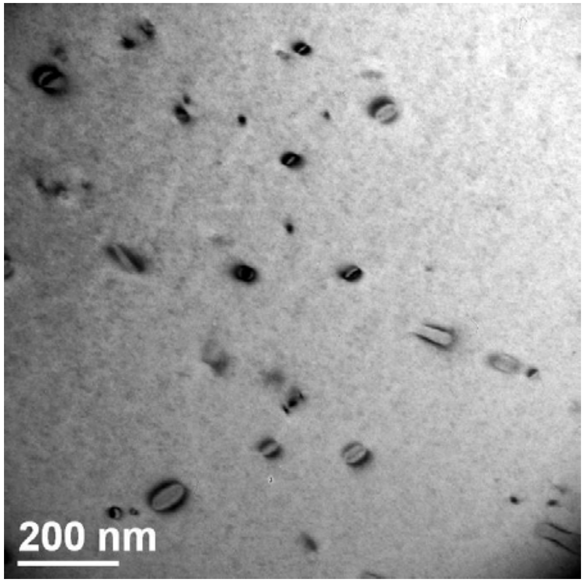


600 ºC | 800 ºC | 900 ºC | 1125 ºC

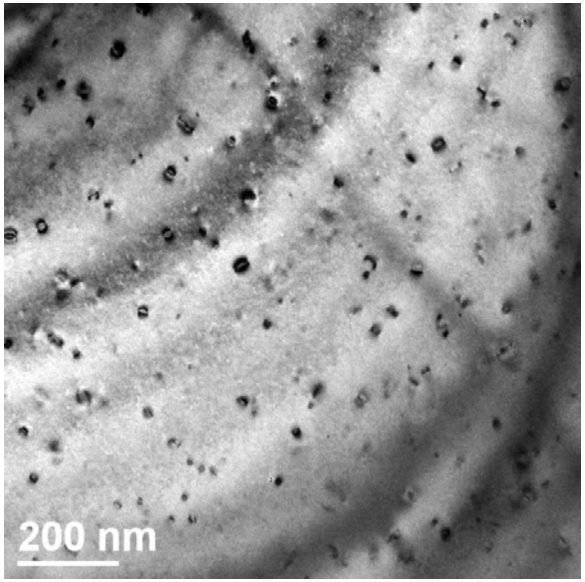
Irradiation leads to changes in the near-boundary regions in the form of defect-denuded zones and the width increase with the temperature (near-stoichometric)

$$L = \sqrt{\frac{C_i^\infty D_i}{P}} \ln\left[\frac{C_i^\infty}{C_i^\infty - C_i^{(L)}}\right] \Longrightarrow D_i = c * L^2(T)$$

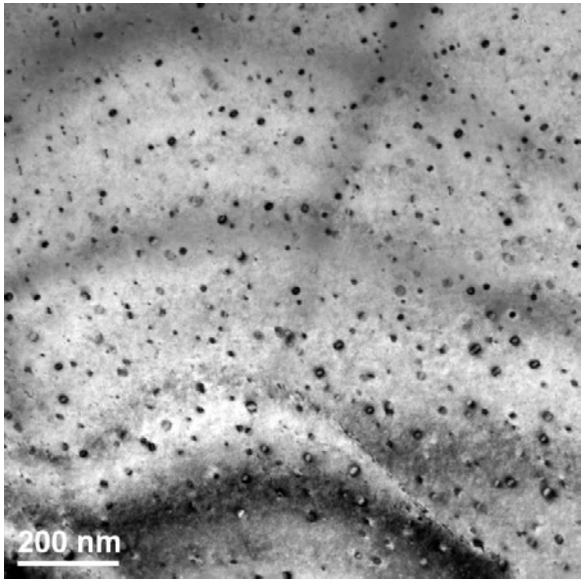
Stoichiometry effect



C/Zr=0.89



C/Zr=0.95

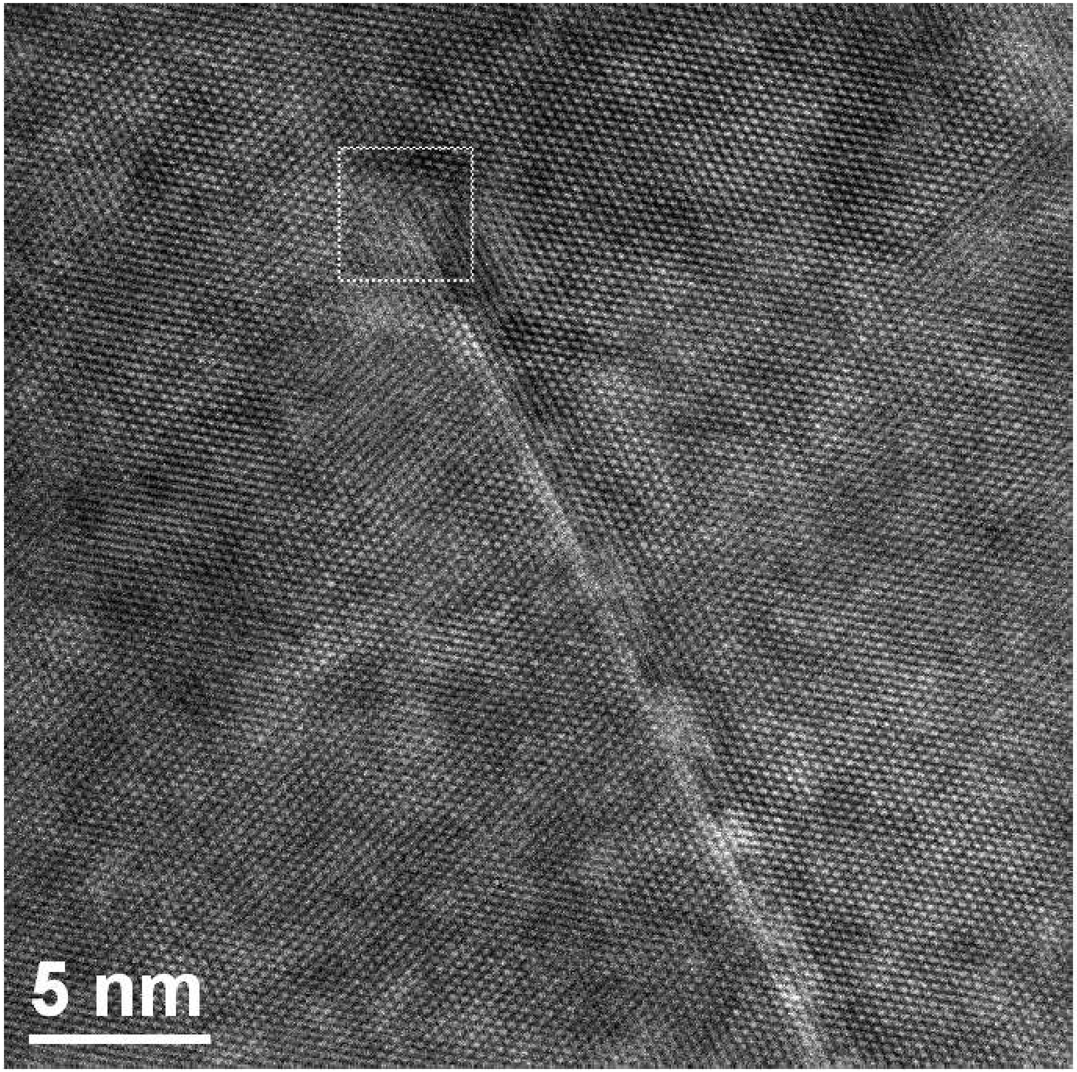


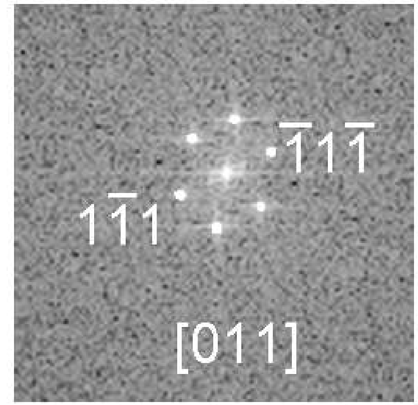
C/Zr=1.05

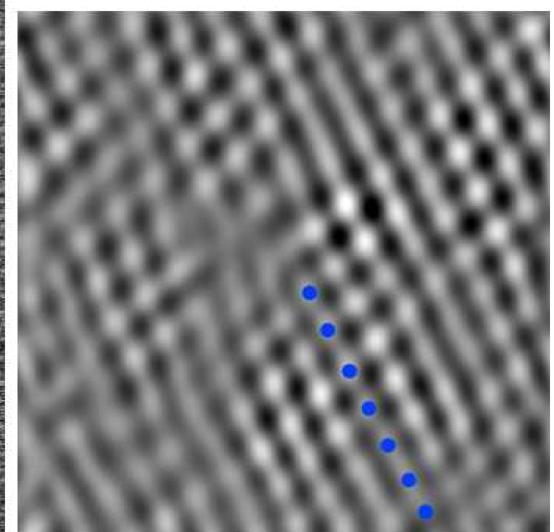
Size of dislocation loops ←

Loop density →

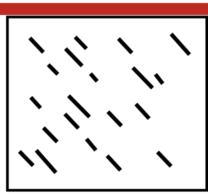
HR-TEM Images of DL (2 dpa, 1125 ºC)





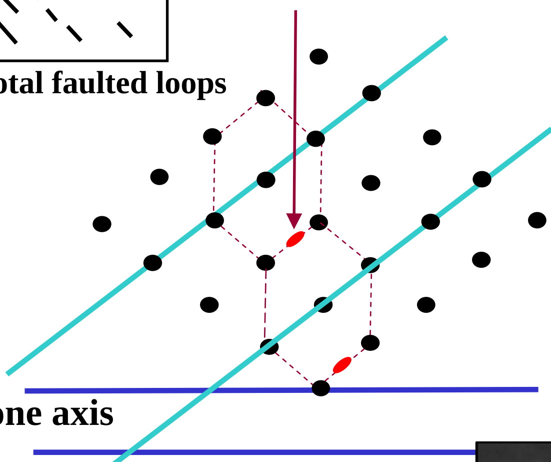


Rel-rod image of Frank Loops in ZrC

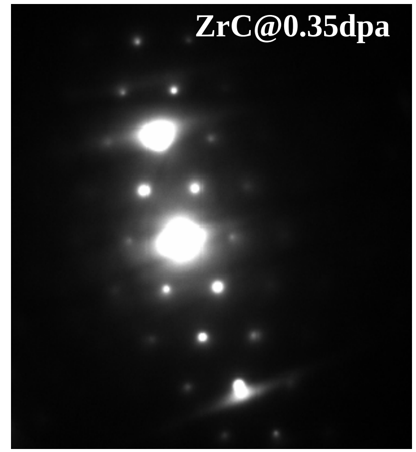


¼ of total faulted loops

Rel-rod streaks from faulted loops on planes [111]

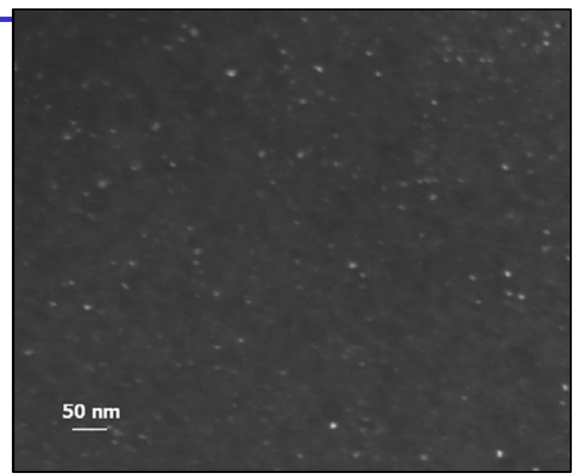


[011] zone axis

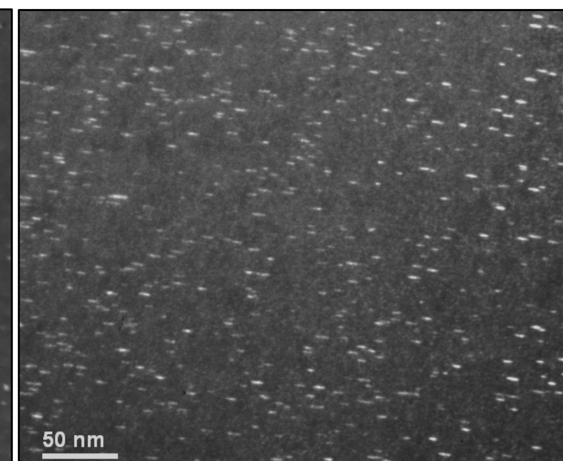


2-beam diffraction patterns near z=[011]

Fault loops in FCC can be treated as a thin platelet HCP structure because of the unique crystallographic relations between FCC and HCP lattice

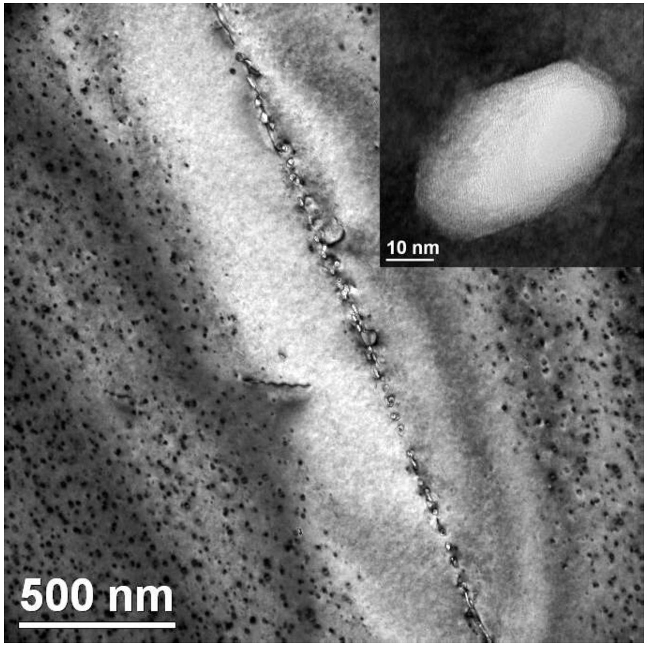


0.35 dpa

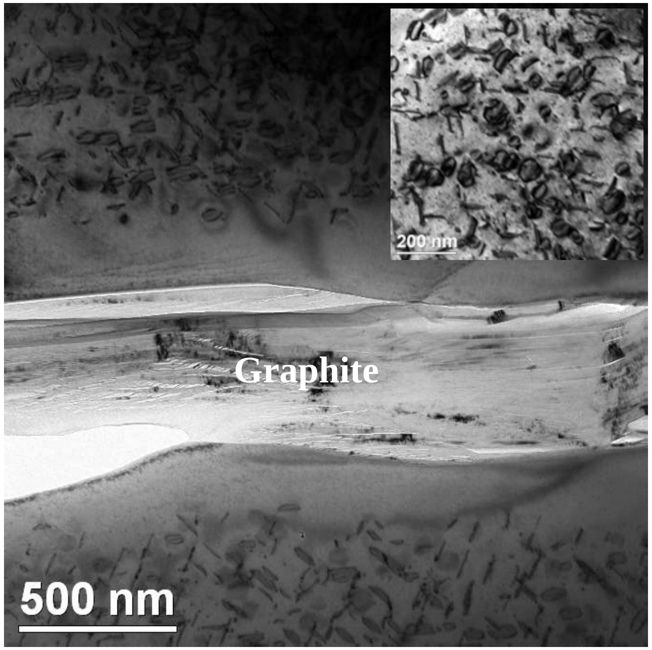


0.75 dpa

Irradiation induced features in hyperstoichiometric ZrC

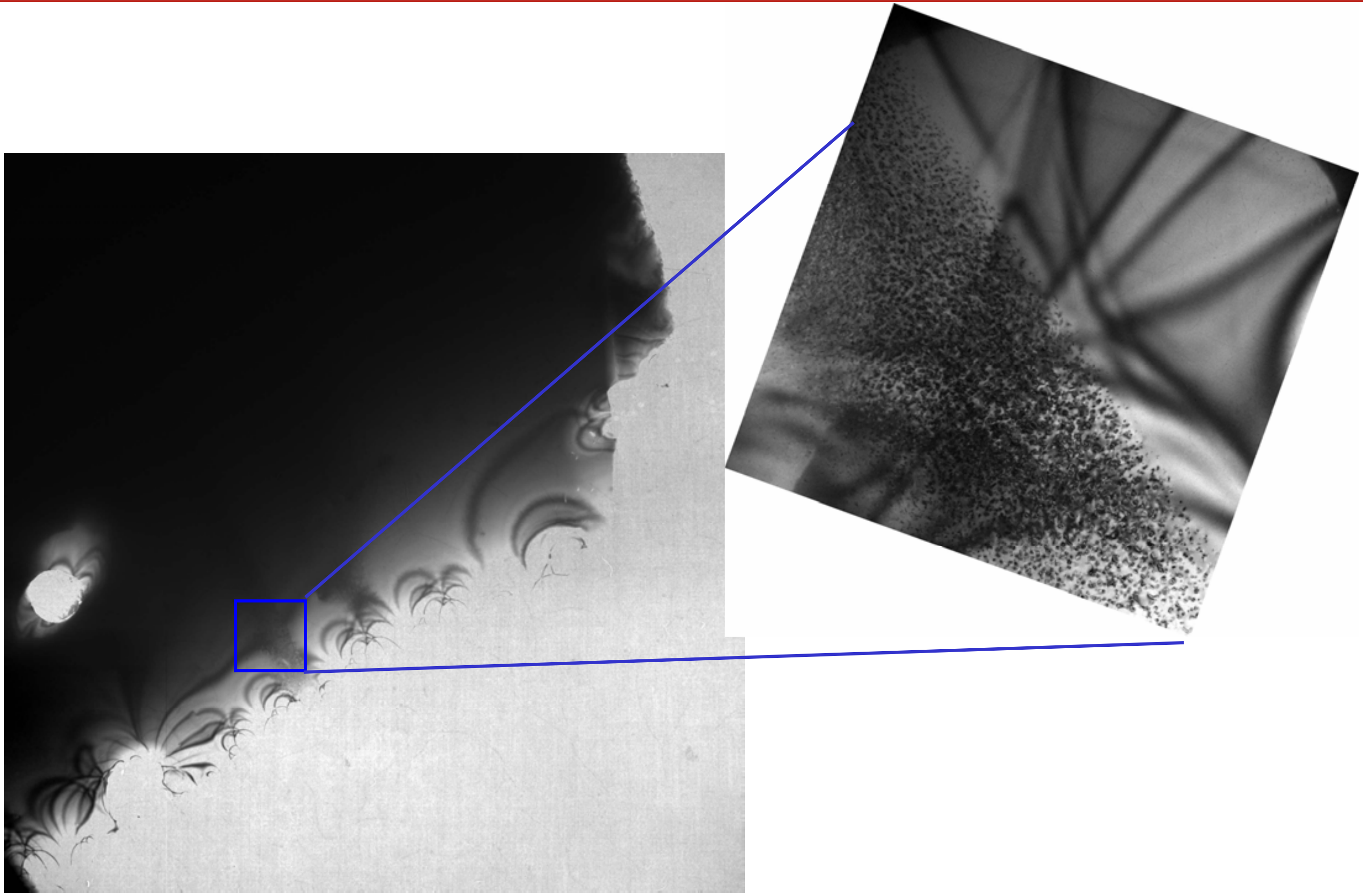


Voids along pre-existing dislocation line in irradiated hyper-stoichiometric $ZrC_{1.05}$



Dislocation loop structure in the vicinity of a graphite precipitate in the irradiated $ZrC_{1.17}$

Cross-sectional TEM, 1125 ºC

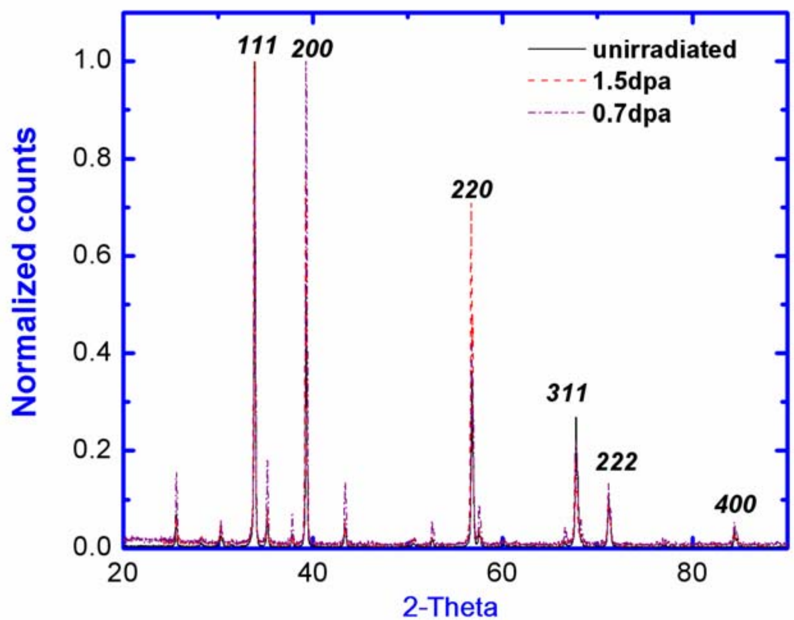


Peak region in irradiated zone-refined ZrC (C/Zr=0.89), where the dose equals to ~20 dpa, no irradiation voids were observed

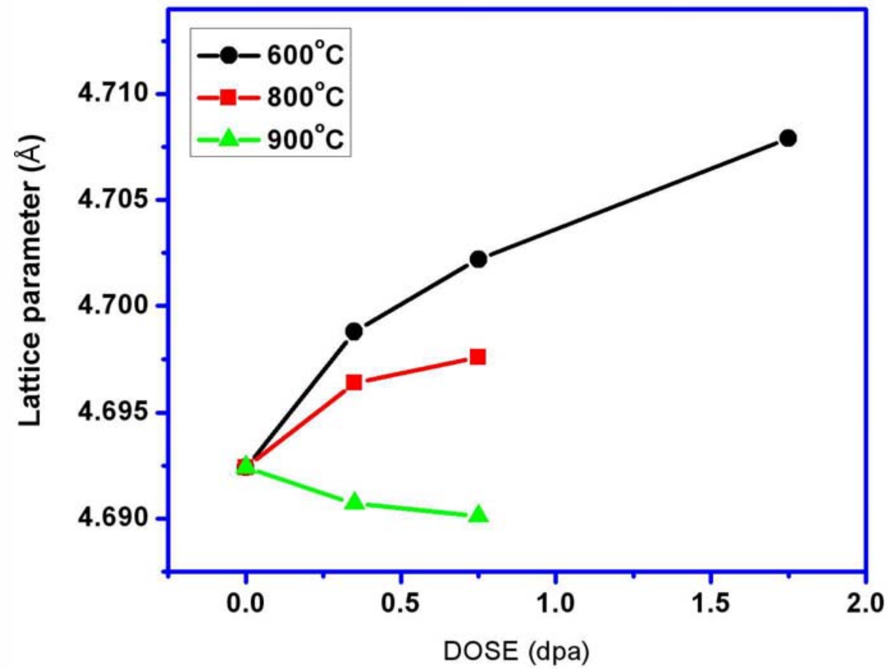
Summary on the microstructural evolution

Mat.	Conditions		Dislocation loops			Voids/bubbles
	Temp (ºC)	Dose (dpa)	Density ($x10^{23}m^{-3}$)	Mean size (nm)	Type	
CERCOM (C/Zr=1.01)	600	0.35	2.7	<1	FL	N
		0.7	3.5	3.5±0.6	FL	N
		1.75	5.7	3.97±0.3	FL	N
	800	0.35	0.22	4.3±0.5	FL	N
		0.7	3.37	5.8±0.56	FL	N
	900	0.35	Na	na		N
		0.7	0.24	10.6±0.4	PL	Along GB
Zone-refined C/Zr=0.84	1125	2	0.026	10.23±0.3	PL	
C/Zr=0.89	1125	2	0.0029	31.7±1.8	PL	N
C/Zr=0.95	1125	2	0.015	14.6±0.6	PL	
C/Zr=1.05	1125	2	0.079	17.9±0.9	PL	Along GB and DL
C/Zr=1.17	1125	2	0.021	56.33±1.3	PL	N

XRD Characterization on Lattice change



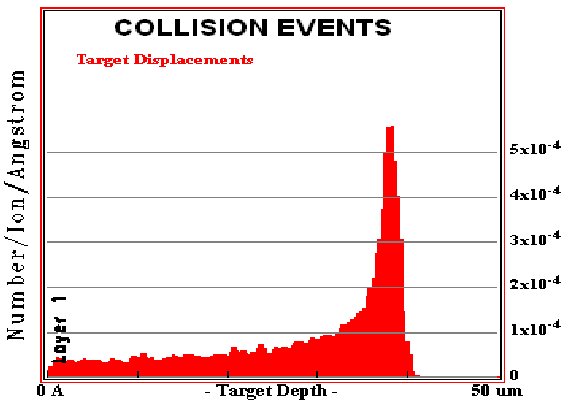
Typical XRD pattern for ZrC

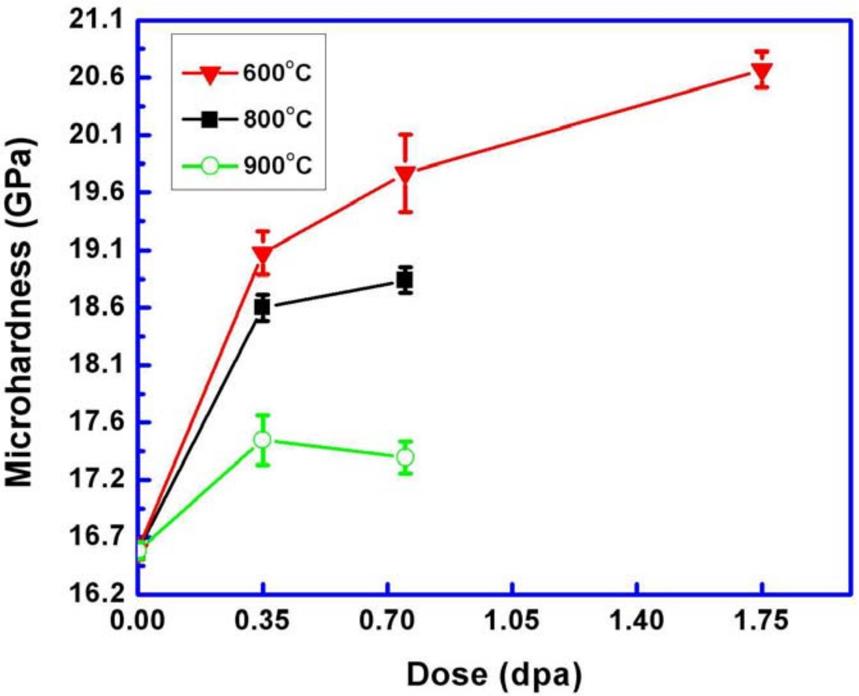


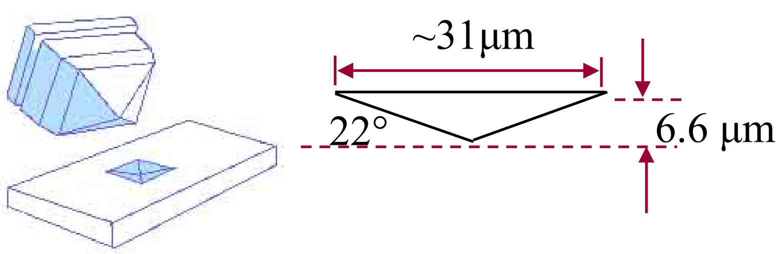
Peak shifts to lower or high 2-theta values indicate lattice expansion or contraction due to irradiation

Microhardness-hardening

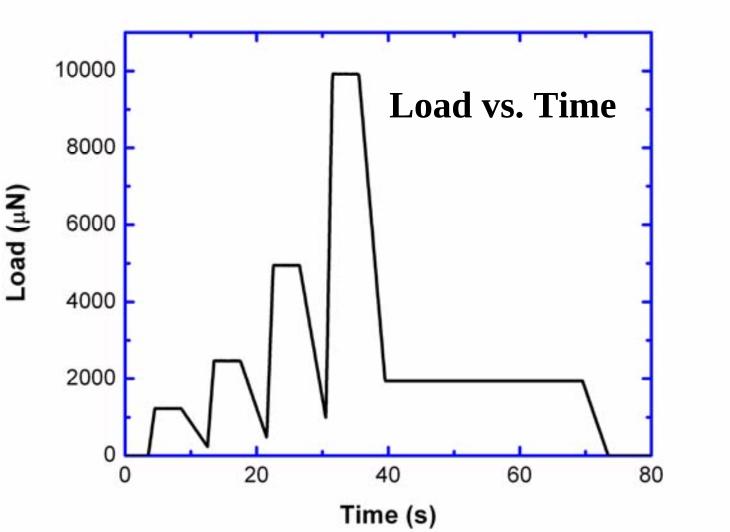
SRIM Simulation of collision events vs. depth in ZrC

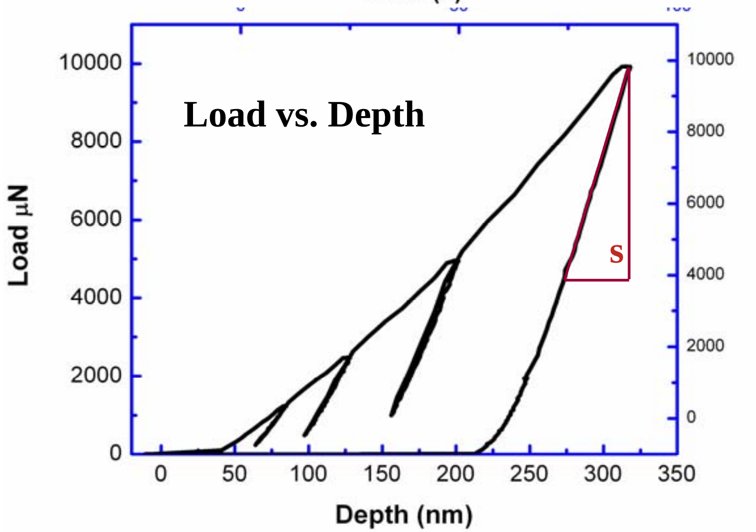


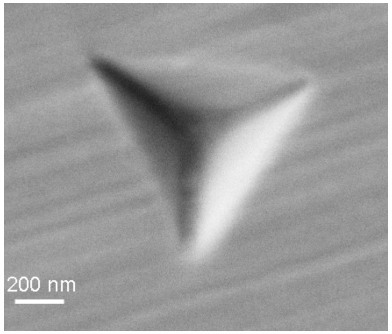




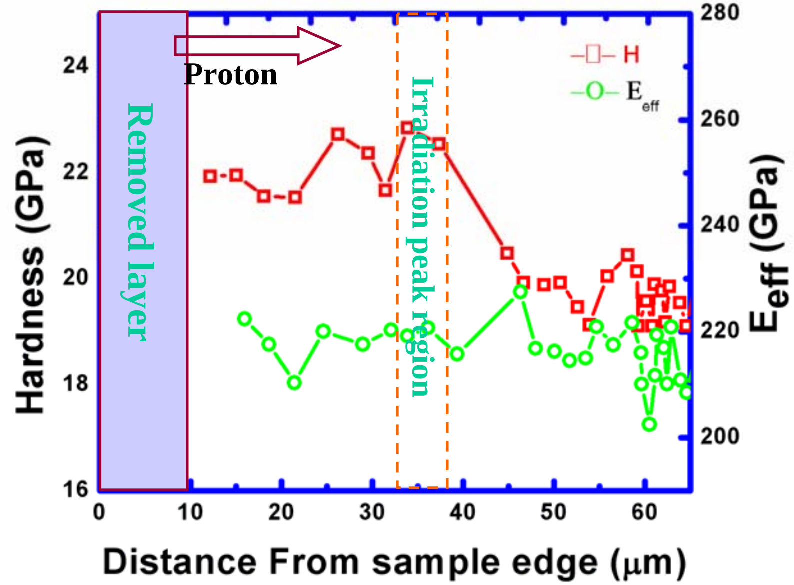
Nano-indentation on irradiated ZrC





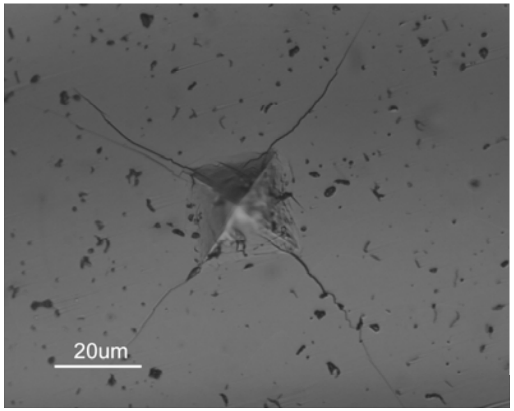


Impression from nano-indentation

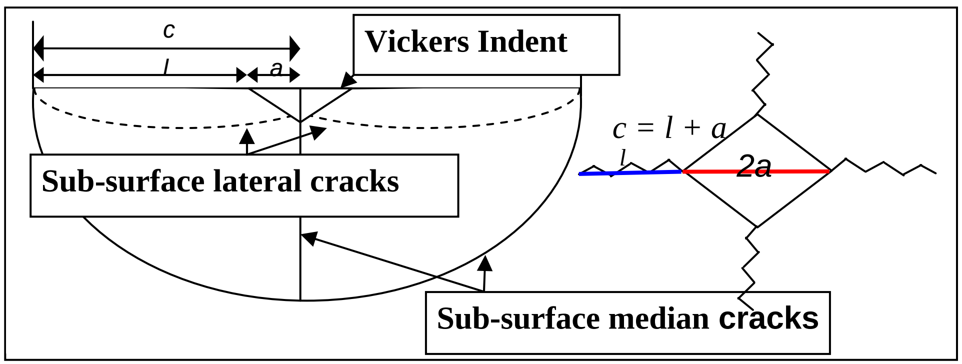


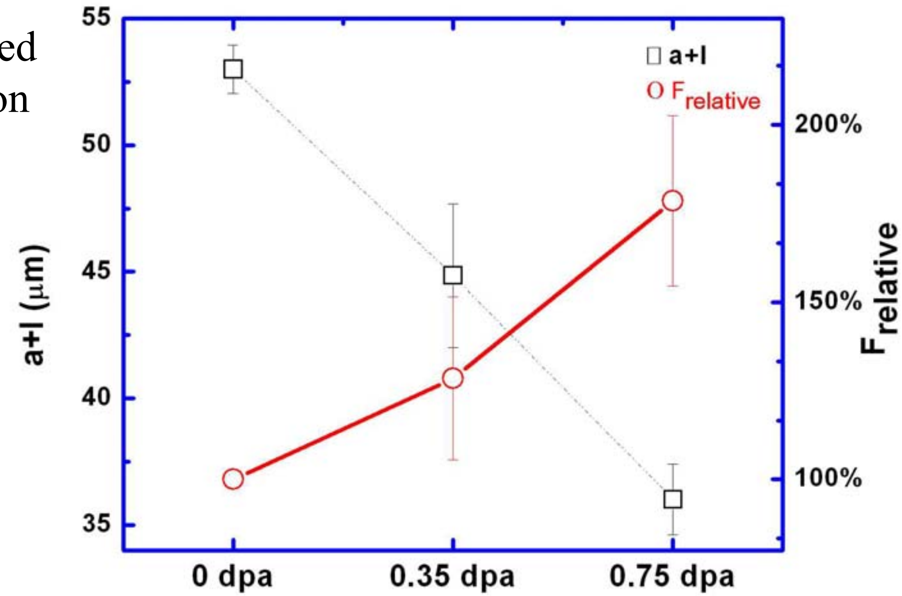
Hardness and Effective **Young's Modulus** variation along the irradiation depth in ZrC with 0.75 dpa at 800 ºC

Fracture Toughness (Micro-indentation)



Crack system produced from microindentation

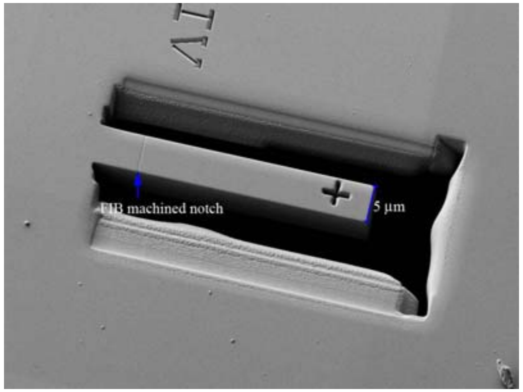


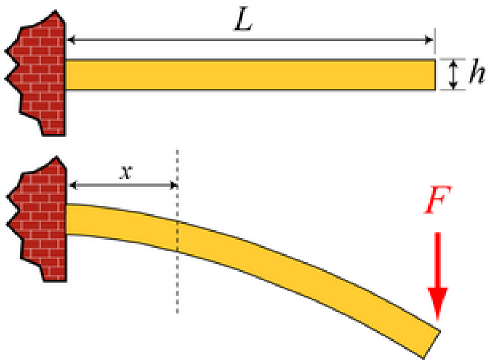


Fracture toughness changes vs. dose at 800 ºC

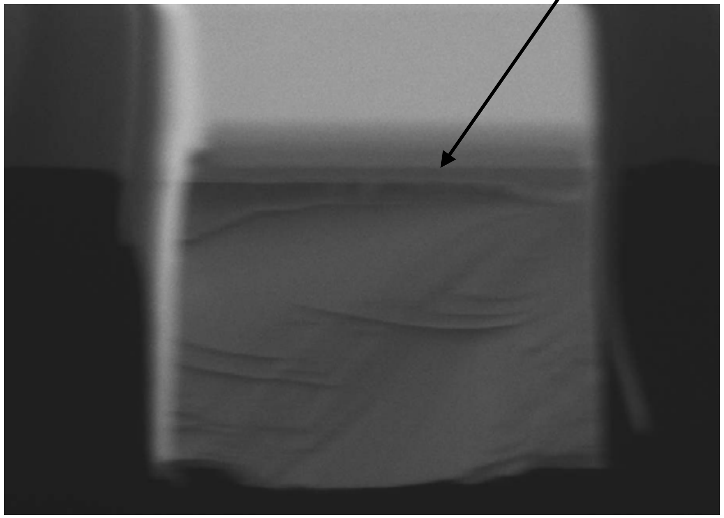
$$F_{Relative} = \frac{K_{IC}}{K_{ICo}} = \frac{c_o^{\frac{3}{2}}}{c^{\frac{3}{2}}} = \frac{(a_o + l_o)^{\frac{3}{2}}}{(a + l)^{\frac{3}{2}}}$$

Fracture Toughness (Micro-cantilever)

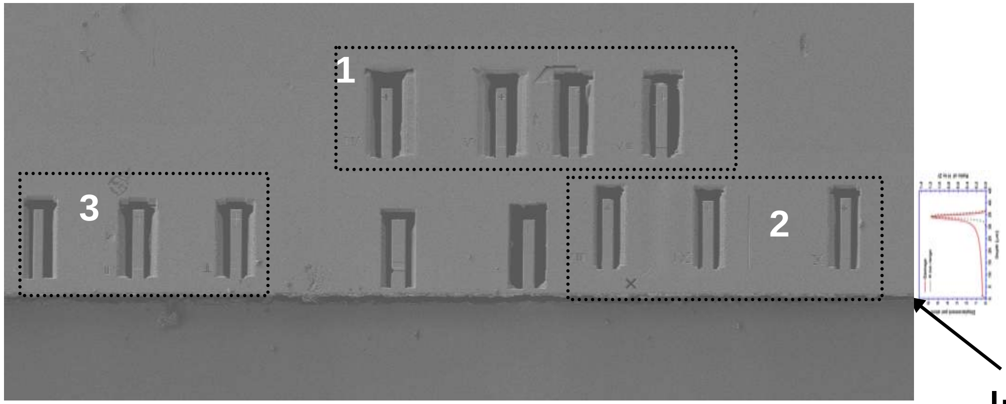




Pre-crack



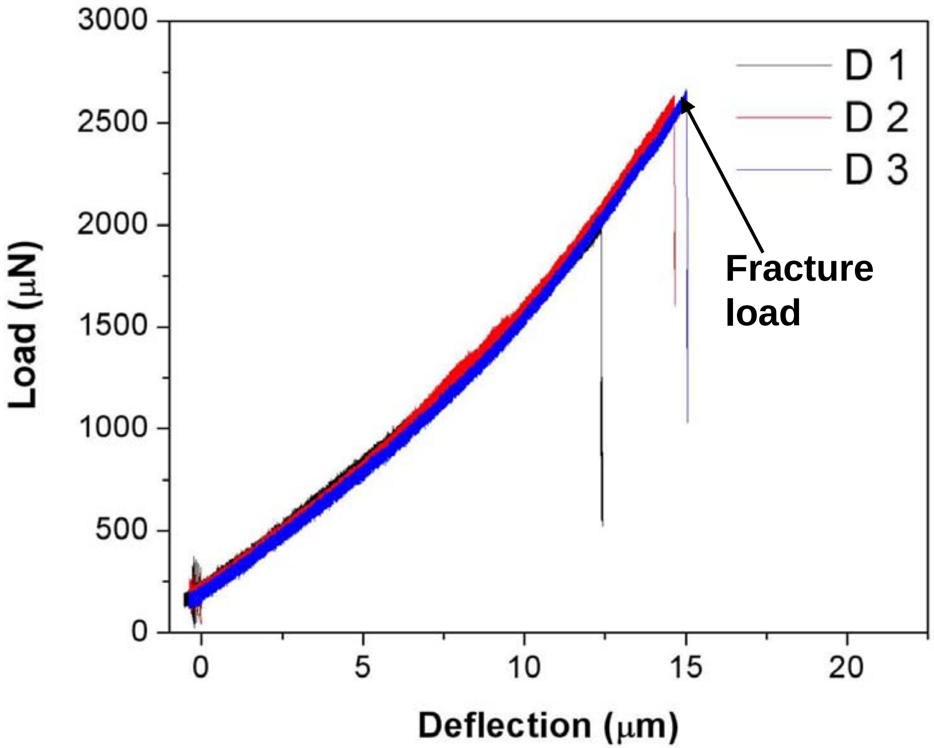
Fractography: cleavage facets



Irradiated surface

Fracture the micro-cantilever using a nanoindenter (Ti 950 Triboindenter, Hysitron)

Fracture Toughness (Micro-cantilever)



Fracture toughness can be calculated using:

$$K_{Ic} = \frac{6PL}{bh^2}\sqrt{\pi a}\,F\left(\frac{a}{h}\right)$$

where *P* is the load at fracture, *L* is the distance between the notch and the loading point, and *b* is the beam width, *h* is the thickness of the beam, and *a* is the depth of the notch.

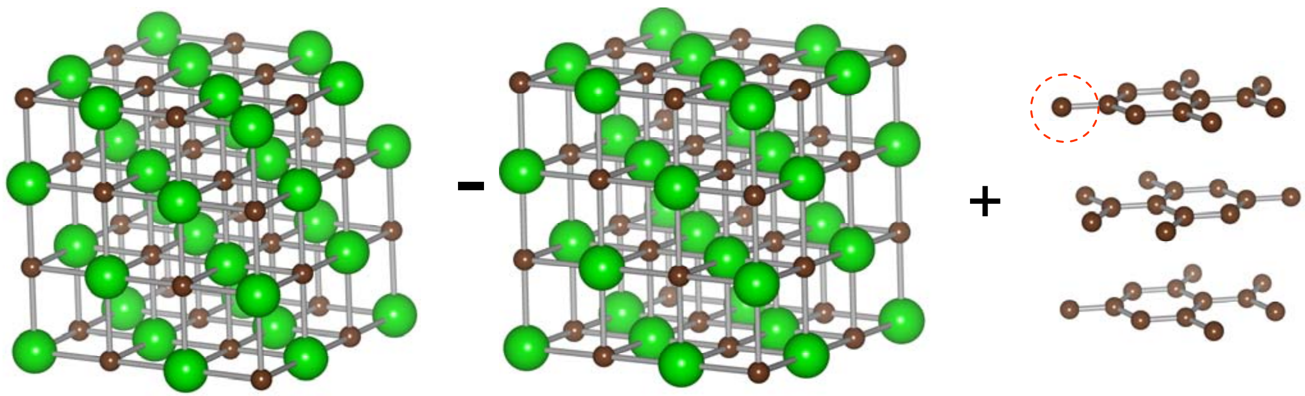
$$F\left(\frac{a}{h}\right) = 1.12 - 1.39\left(\frac{a}{h}\right) + 7.32\left(\frac{a}{h}\right)^2 - 13.1\left(\frac{a}{h}\right)^3 + 14.0\left(\frac{a}{h}\right)^4$$

~30% increment in fracture toughness !

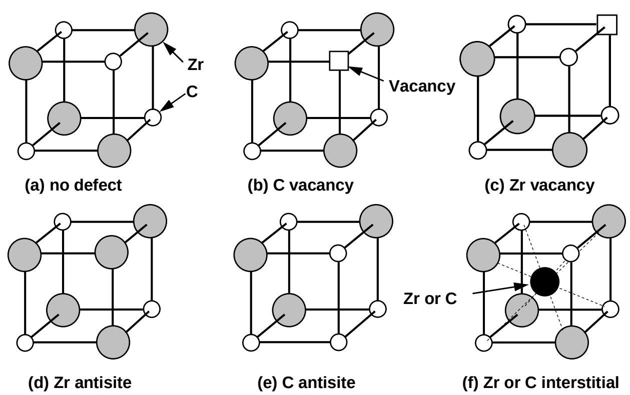
Point Defect Formation Energy Calculation

$$Zr_{32}C_{32} \rightarrow Zr_{32}C_{31} + C_{Graphite}$$

E_{V_C} =



64-atom supercell, k-points 4x4x4, Ecut=16 Hartree, Vienna Ab-initio Simulation Package (VASP) has been utilized to run the **ab initio calculation.**



Summary on the point defect formation energy

- Carbon vacancy has the lowest formation energy
- Carbon antisite has the highest formation energy
- Carbon interstitials can position along [101], [111] and [100] directions. while the lowest energy of carbon interstitials is in [101] direction with energy of 3.56 eV/defect
- The most stable Zr interstitial is the tetrahedral site found along the [111] direction with energy of 8.72 eV/defect

Defect	C_v	Zr_v	Zr_C	C_{Zr}	C_i	Zr_i
Energy (eV)	**0.93**	**8.54**	**7.93**	**11.36**	**5.46**	**8.72**

Conclusions

- The microstructure of proton irradiated ZrC at 600-1125ºC is dominated with dislocation and dislocation size and density increases with dose, but the density decreases vs. temperature.
- Voids along GB and DLs were only observed in hyper-stoichiometric ZrC irradiated at 1125 ºC, and the sub-stoichiometric ZrC demonstrates a relatively enhanced radiation damage resistance.
- Proton irradiation caused hardening, as well as the increment in fracture toughness.
- Carbon vacancies and interstitials are energy favored point defects based on atomistic calculation.