Course goal: Recall the development of different Zr alloys, containing different alloying additions, and explain the role of specific thermomechanical stages for refining microstructure.

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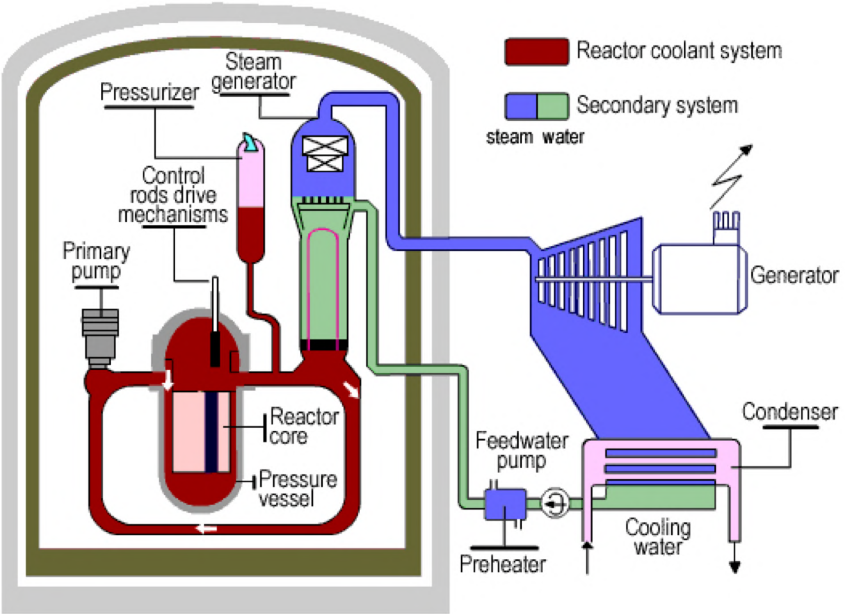
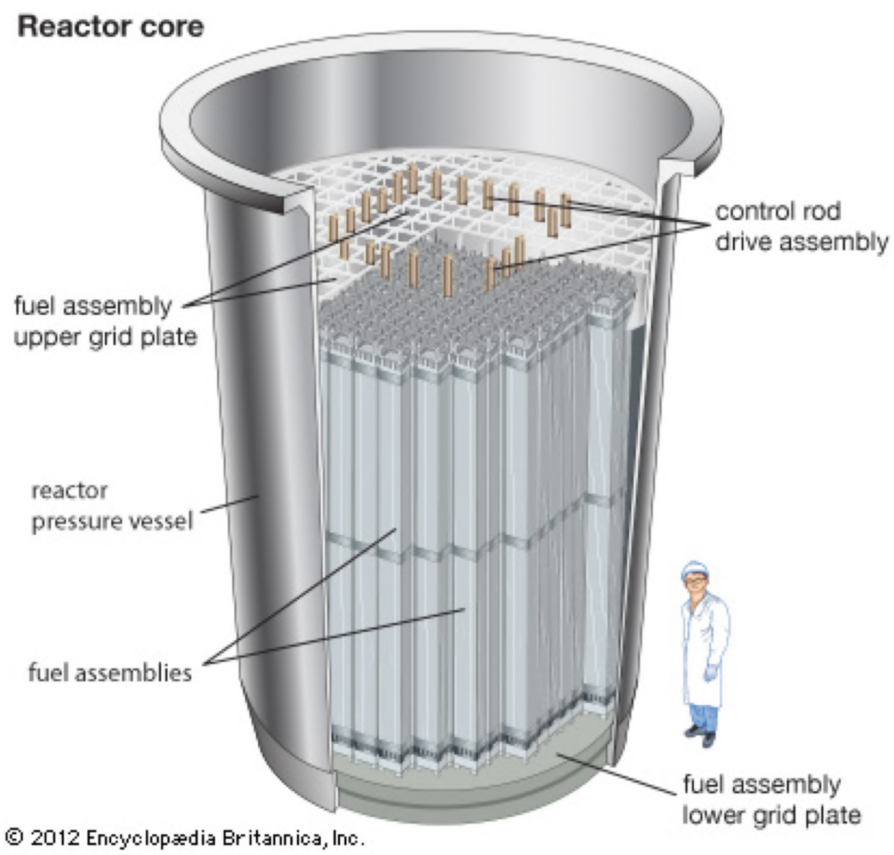
- Describe the fabrication process for Zr cladding, including the pilgering process.
- Explain how changes in processing and annealing of Zr materials might affect the in-reactor performance.

Alloy	Cr	Fe	Nb	Ni	Sn
Zircaloy-2	0.10	0.17	<0.01	0.07	1.35
Zircaloy-4	0.10	0.17	<0.01	<0.01	1.24
ZIRLO™	<0.01	0.09	0.87	<0.01	0.92
Low-Sn ZIRLO™	<0.01	0.09	0.92	<0.01	0.66
Zr-1.0%Nb-0.0%Sn e.g. (M5)	<0.01	0.08	0.91	<0.01	0.01

Table showing the general trends in alloy additions for different Zr alloys over time.

Applications of Zr Alloys





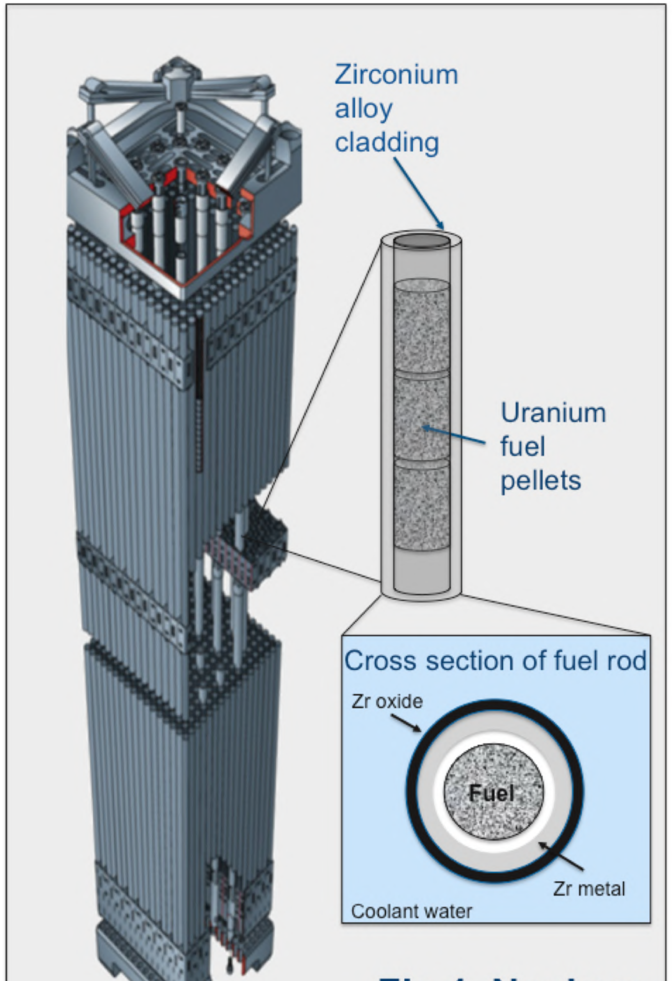
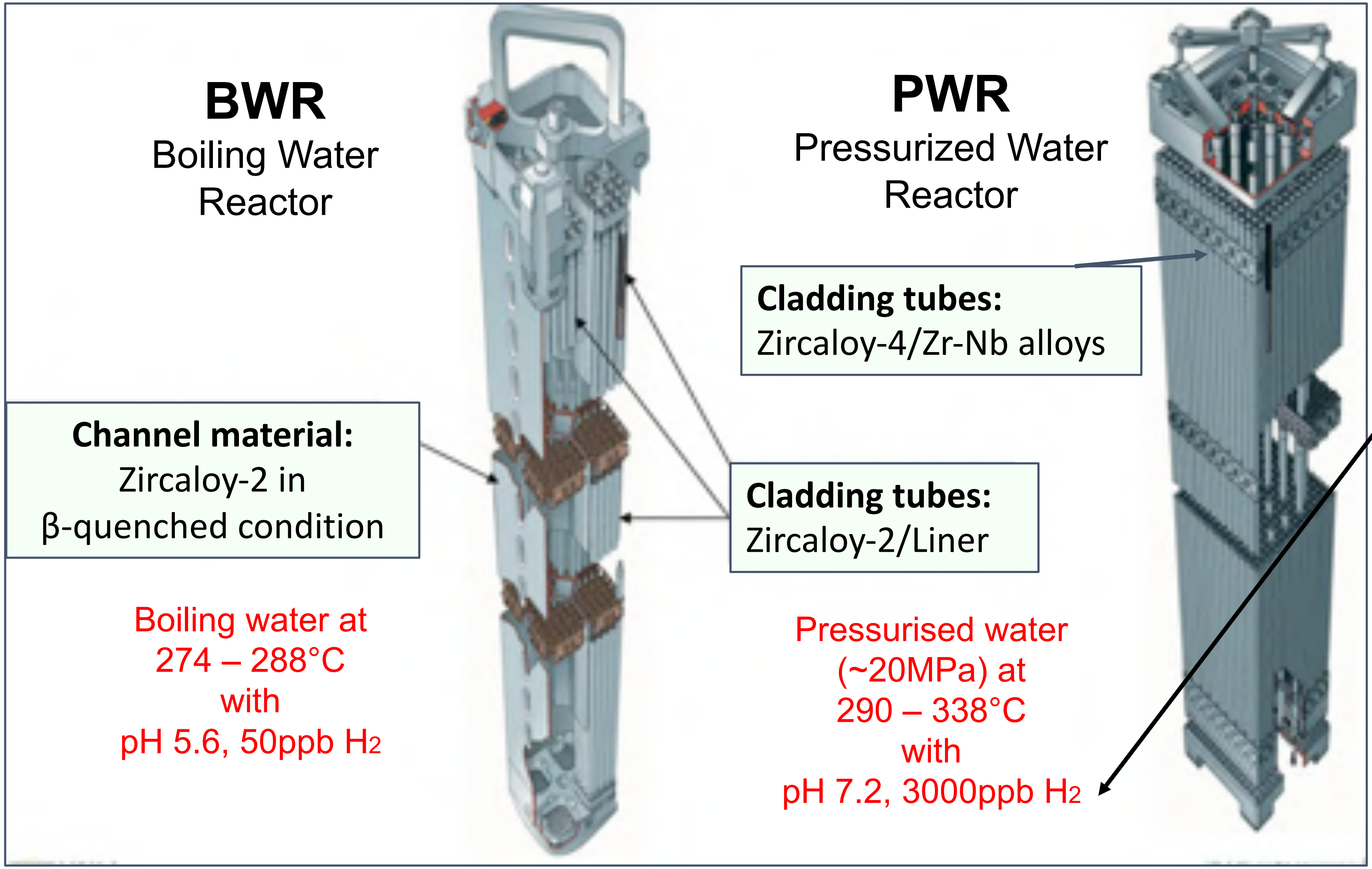


Fig.1. Nuclear fuel assembly[1]

Applications of Zr Alloys

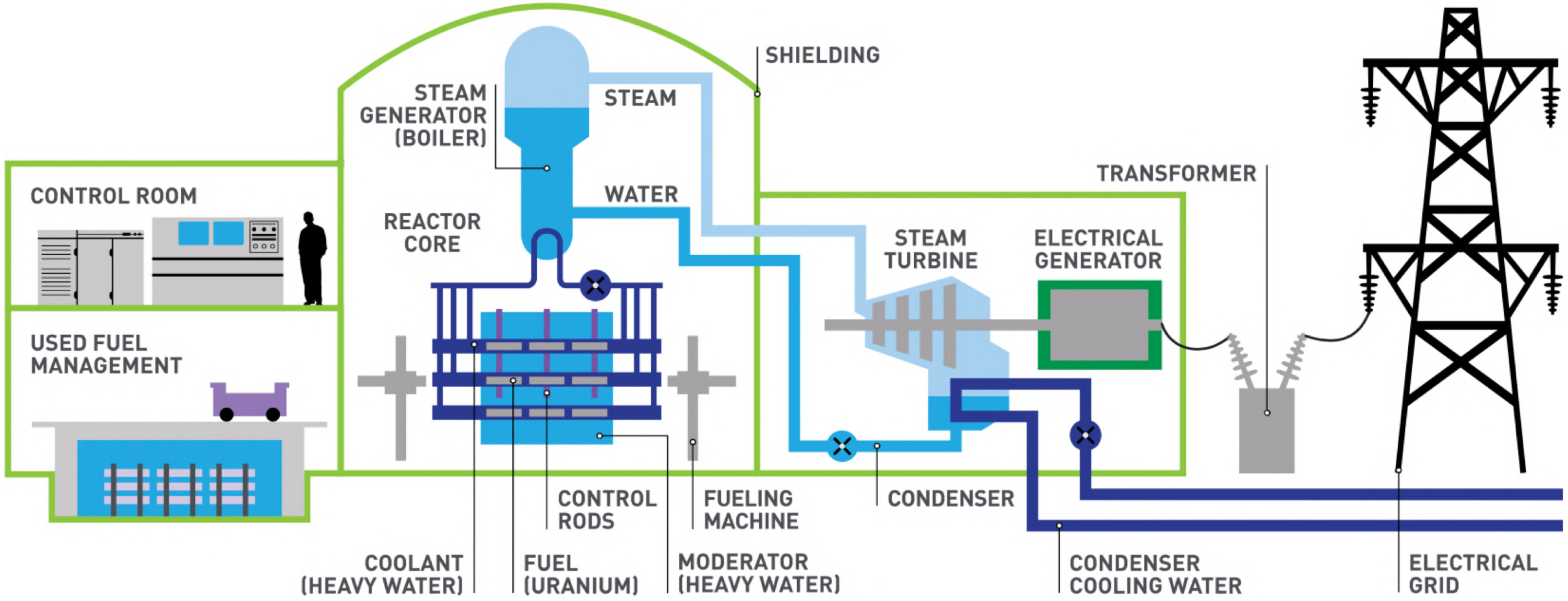


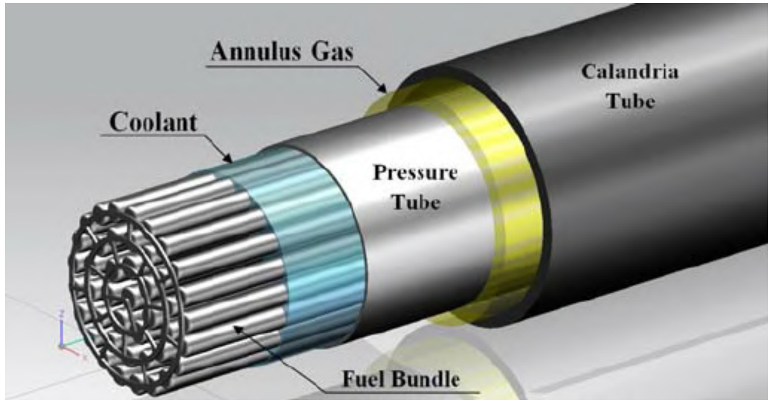
Radiolysis of water → oxidation. So, H_2 added to minimise radiolysis.

Primary water also usually has additions of 2 wt.ppm of LiOH (to control PH) and 1000 wt.ppm of H_3BO_4 (to control reactivity)

Applications of Zr Alloys

- Two-phase Zr-Nb alloys also used as pressure tubing in CANDU (Canadian Deuterium Uranium) reactors.

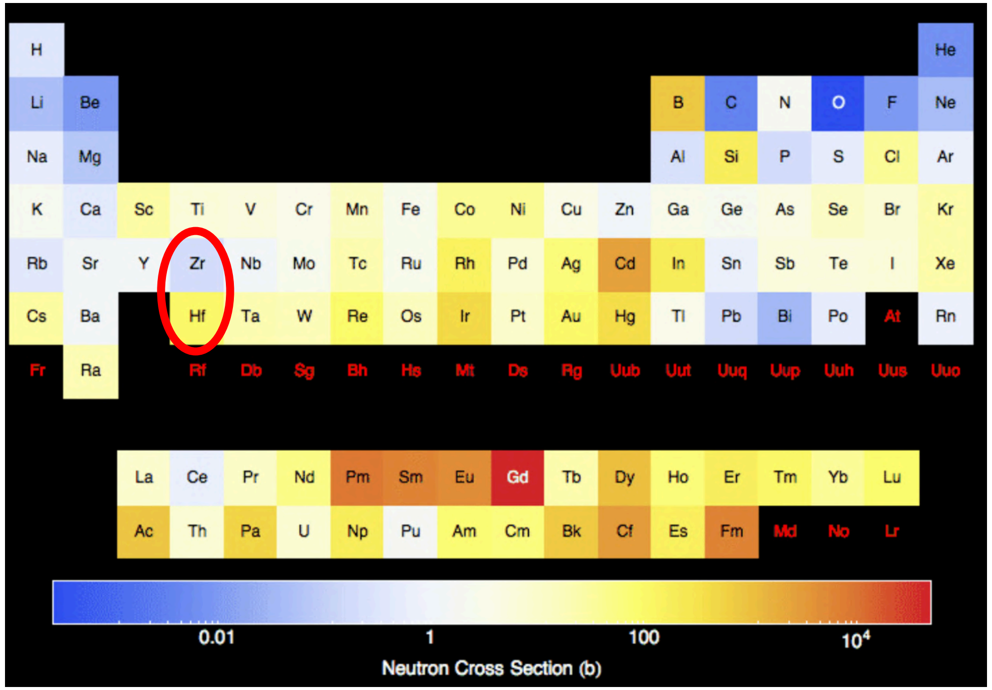




Properties of Zr Alloys

- Corrosion resistance (goodish)
- Irradiation damage resistance (ok)
- Mechanical properties (adequate)
  - Strength
  - In-reactor creep behaviour
- Neutron transparency (v. good)

Good Combination of properties



Neutron Cross Section (b)

History of Zr Alloy Development

- Pure Zr found to have poor corrosion properties

- Various additions investigated.
- Sn chosen to reduce N impurities.

→ corrosion resistance, high solid solution, good mechanical properties.

- **Zircaloy-1** Zr-2.5%Sn *(1952)*

- Problems with Hf separation

- Zr alloys had low ductility and large neutron capture cross-section.

→ solved along with Kroll process *(identical to Ti production).*

- Development of Nuclear Submarines

- Strong driver for the development of Zr alloys.

- **Zircaloy-2** Zr-1.5Sn-0.3Fe/Cr/Ni

- Zircaloy-1 + "accidental contaminant?" *(hint: contains Sn, Fe, Cr, Ni)*
- Dramatic improvement in corrosion resistance.

History of Zr Alloy Development

- **Zircaloy-3**
- Reduced Sn, increase Fe.
- Unsuccessful development with poorer performance.

- **Zircaloy-4**
- Ni-free variant of Zircaloy-2

→ Reduced hydrogen ingress, important for PWRs
- Now mainly used in nuclear submarines.

- **Today: Zr alloys with Nb additions**
- Originally developed in Russia.
- **Zr-2.5Nb** – high strength two-phase Zr alloy for pressure tubes in CANDU reactors.
- **ZIRLO** (Zr-1Nb-1Sn-0.1Fe)
- *Future → less Sn?*
- **Low Sn ZIRLO** (Zr-1Nb-0.7Sn-0.1Fe)
- **M5** (Zr-1Nb) – *no Sn?*

Alloying elements in Zr-alloys

- **Sn**: (typically 0-1.4 wt.%), stabilises α-phase, originally mitigated nitrogen impurity issues, increases yield stress/creep resistance, but reduces corrosion resistance.
- **Nb**: (typically 0-2.5 wt.%), stabilises β-phase, (solid solution in β but precipitates in α), increases yield strength, creep properties and corrosion resistance.
- **Fe, Cr, Ni**: (0.05-0.2%) stabilises β-phase (solid solution in β but precipitates in α), seem to increase corrosion resistance by formation of second phase particles (SPPs).
- **Oxygen**: (800-1600 ppm), stabilises α-phase (solid solution) and increases yield strength.

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Zr Research Today

- Effect of processing parameters on microstructure and performance
- Texture and precipitates

- Chemical stability in LWR environment.
- Aqueous corrosion.
- Hydrogen pick-up.

- Mechanical stability
- Mechanical properties in service.
- Delayed Hydride Cracking (DHC).
- Pellet Cladding Interaction (PCI).

- Dimensional stability
- Irradiation induced creep and growth.

Increased fuel rod lifetime

i.e. increased energy extraction from fuel assemblies

Course goal: Recall the development of different Zr alloys, containing different alloying additions, and explain the role of specific thermomechanical stages for refining microstructure.

Learning outcomes:

- Recall the history of Zr alloy development and explain the reasons behind trends for increasing/decreasing certain alloying additions.
- ***Recall the fabrication process for Zr cladding, including the pilgering process.***
- Explain how changes in processing and annealing of Zr materials might affect the in-reactor performance.

An extruded Zr alloy tube.

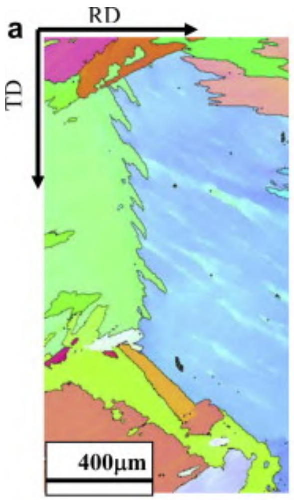
Fabrication of Zr Cladding Material

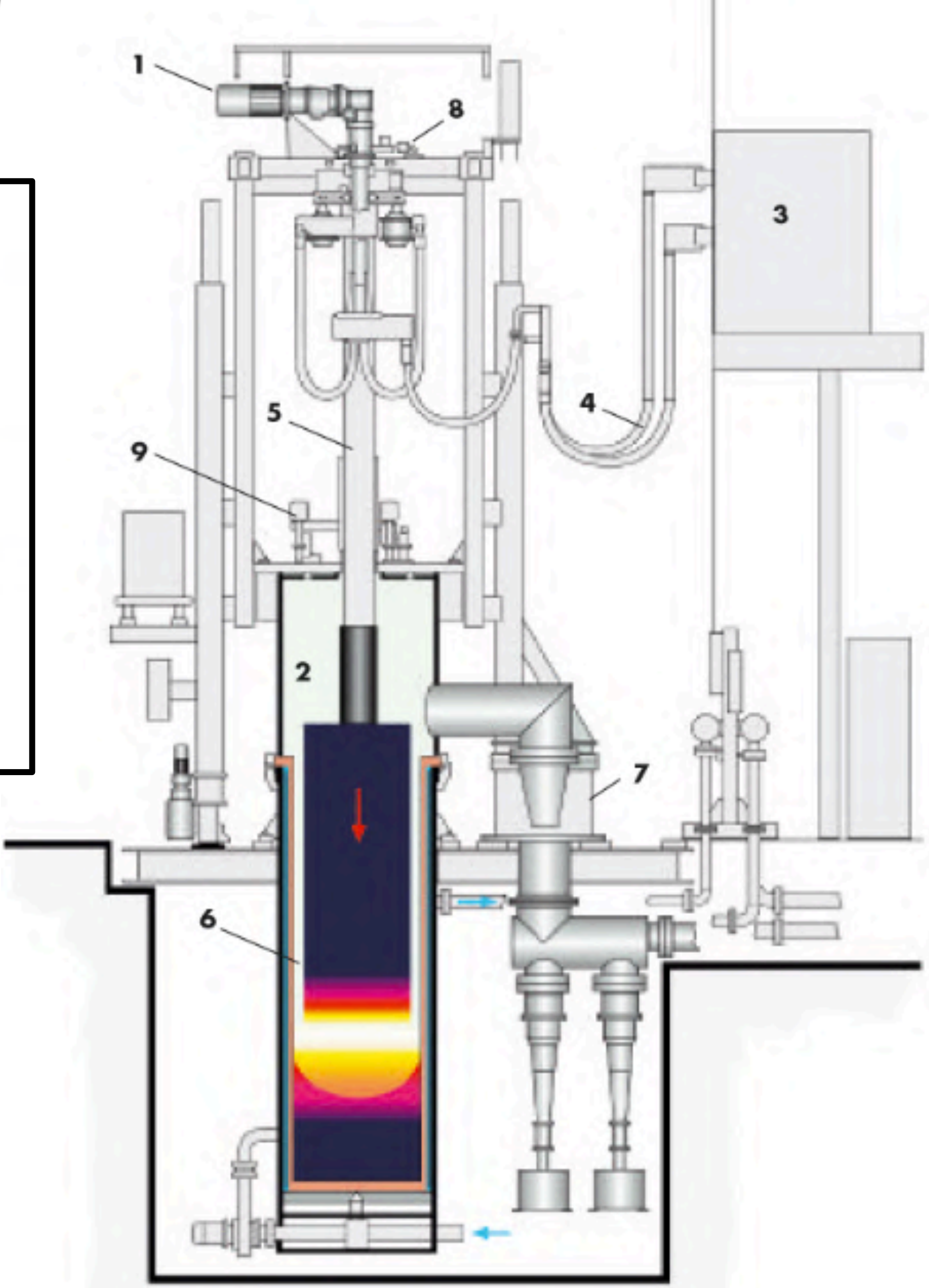
- Zirconium sponge mixed with alloying additions.
- Melted three times in a consumable electrode vacuum arc remelting furnace.
- Why remelt? For chemical homogeneity.
- Increased melts → higher oxygen content.

- *The result is a β-transformed microstructure with a large prior-β grain size a colony packets of α-grains.*

Schematic of the VAR furnace

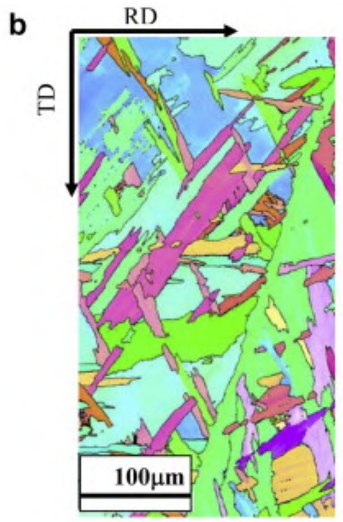
1 Electrode feed drive
2 Furnace chamber
3 Melting power supply
4 Busbars/cables
5 Electrode ram
6 Water jacket with crucible
7 Vacuum suction port
8 X-Y adjustment
9 Load cell system





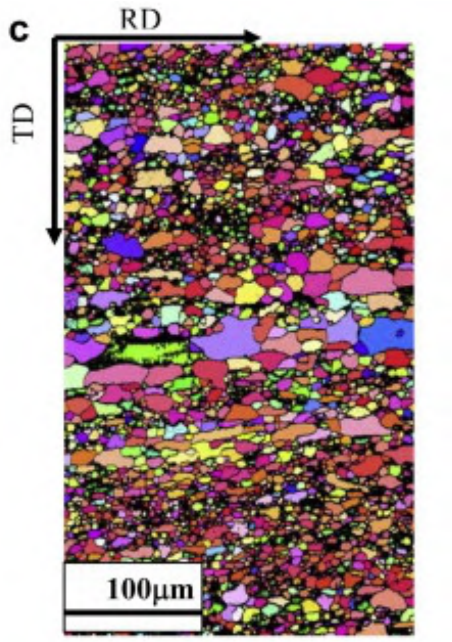
Fabrication of Zr Cladding Material – Forging

- The billet is forged into a rod
- Forging is done at high temperature *(typically in the α + β phase regime)*
- *Forging in this regime begins to break down the large β-grain structures. The material is then annealed to produce a β-annealed microstructure.*

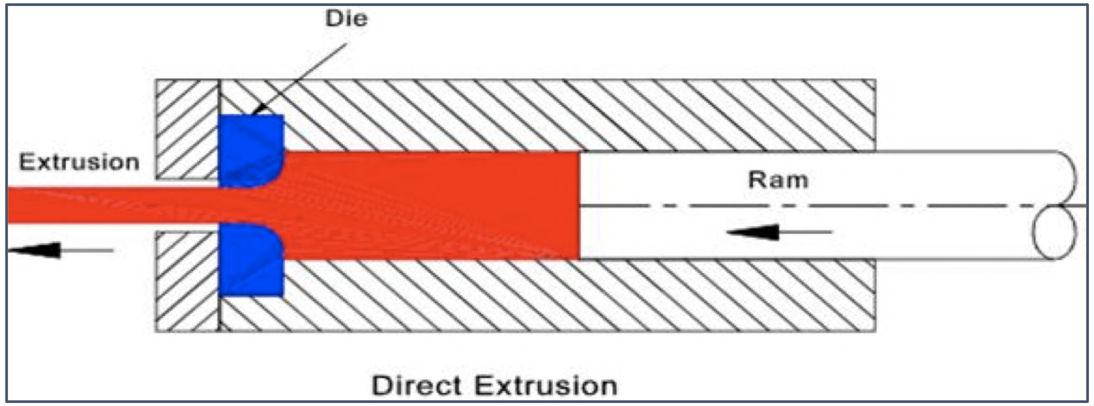


Fabrication of Zr Cladding Material – Extrusion

- A central hole is drilled into the rods.
- This is followed by hot-extrusion of the rods *(typically in the full α-phase regime)*.

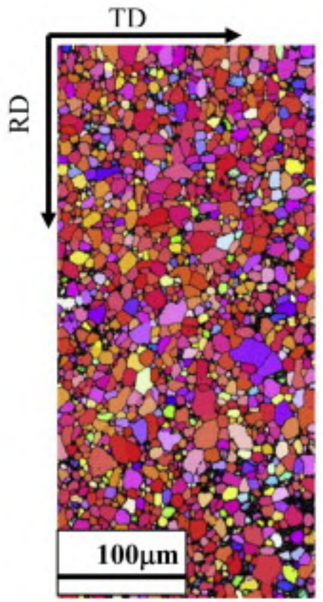


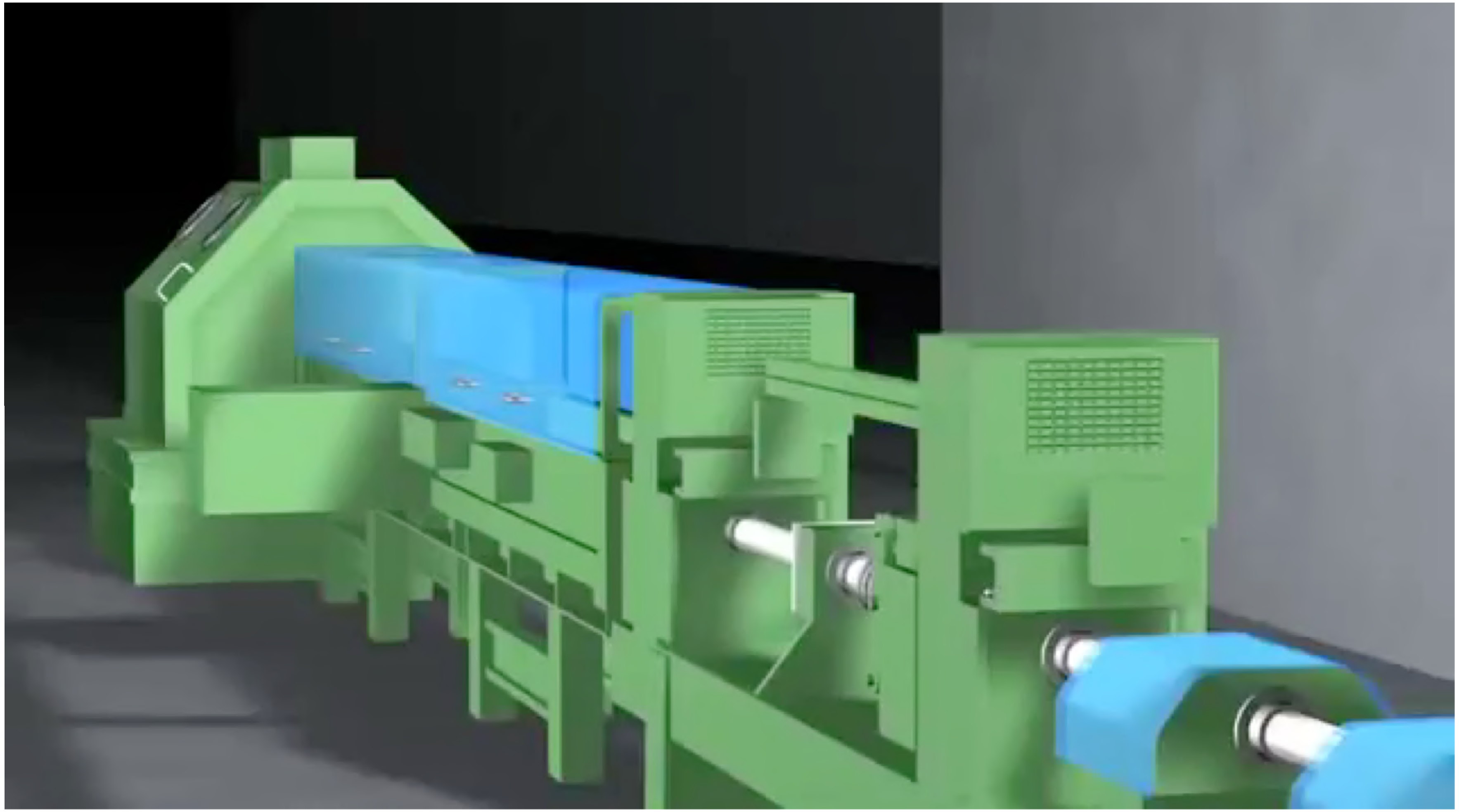
- *Extrusion refines the α-grain size and develops strong textures in the material*



Fabrication of Zr Cladding Material – Pilgering

- Several cold pilgering stages, with intermediate annealing, control the final shape of the cladding rod.
- *Pilgering further refines the α grain size and strengthens texture.*





Microstructural Evolution

As-Cast

Forge and β-quench at 1050°C

Hot Extrusion 825°C (ratio 14:1)

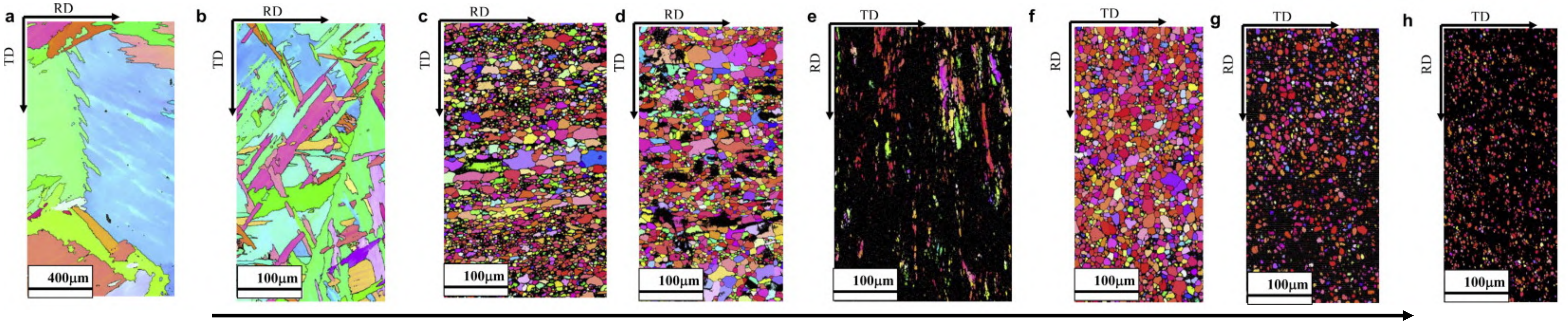
1st Anneal 760°C 4 hours

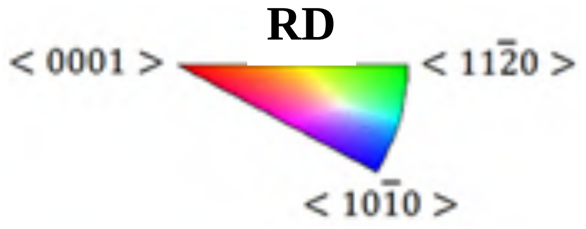
1st Pilger 80% Reduction

2nd Anneal 650°C 4 hours

2nd Pilger 70% Reduction 3rd Anneal 575°C

3rd Pilger 60% Red. Final Anneal 500°C





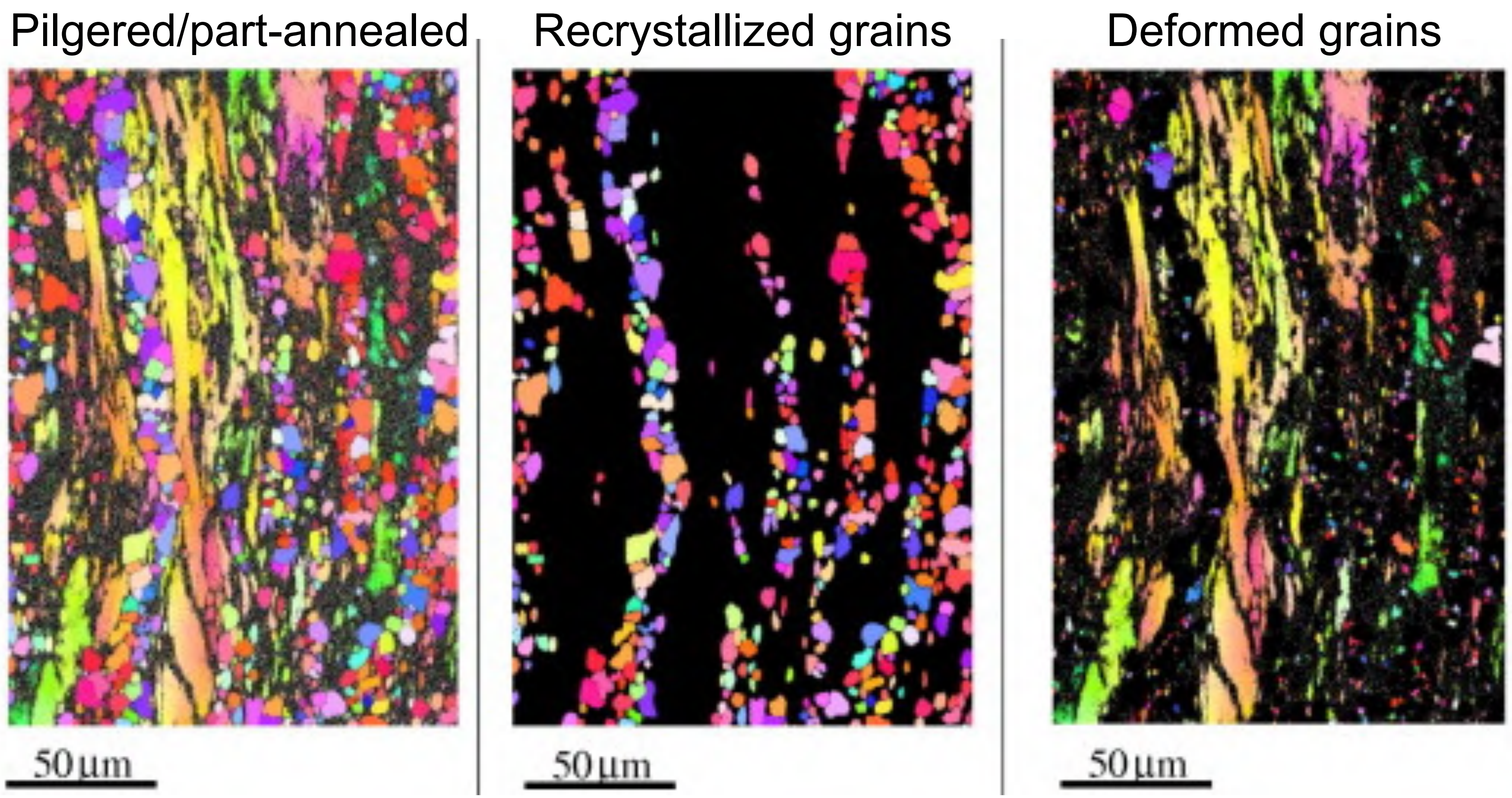
- Why have a fine grain size? For Hall-Petch strengthening and to reduce in-reactor creep

Annealing

- Why do we anneal the cladding materials after pilgering?
- Recrystallization → removal of dislocations.
- Dislocations have significant impact on in-reactor behaviour, affecting;

- In-reactor creep
- Irradiation growth
- Second phase precipitation

etc…



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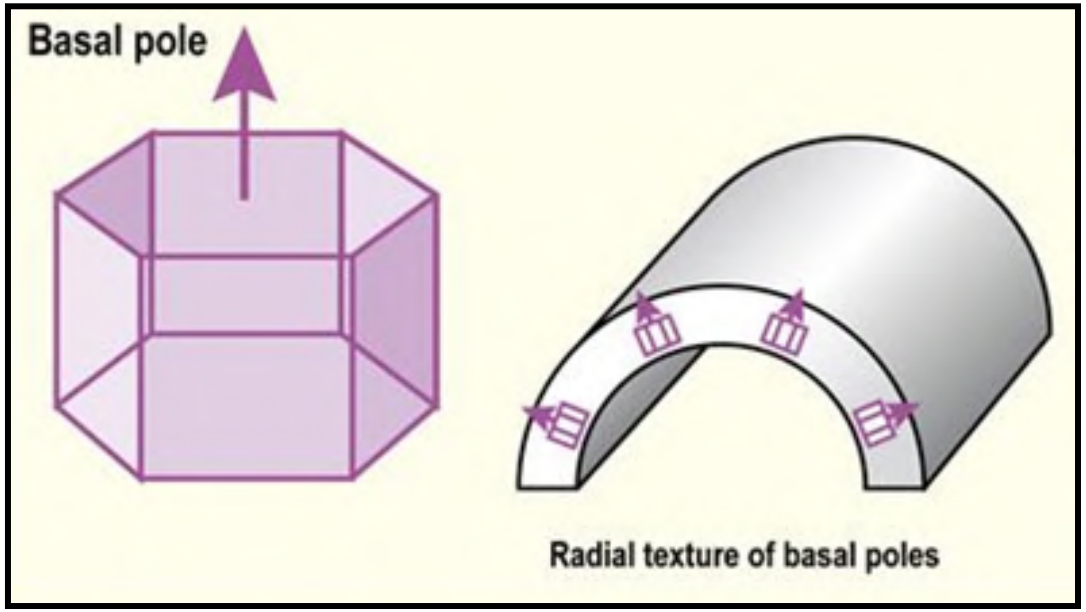
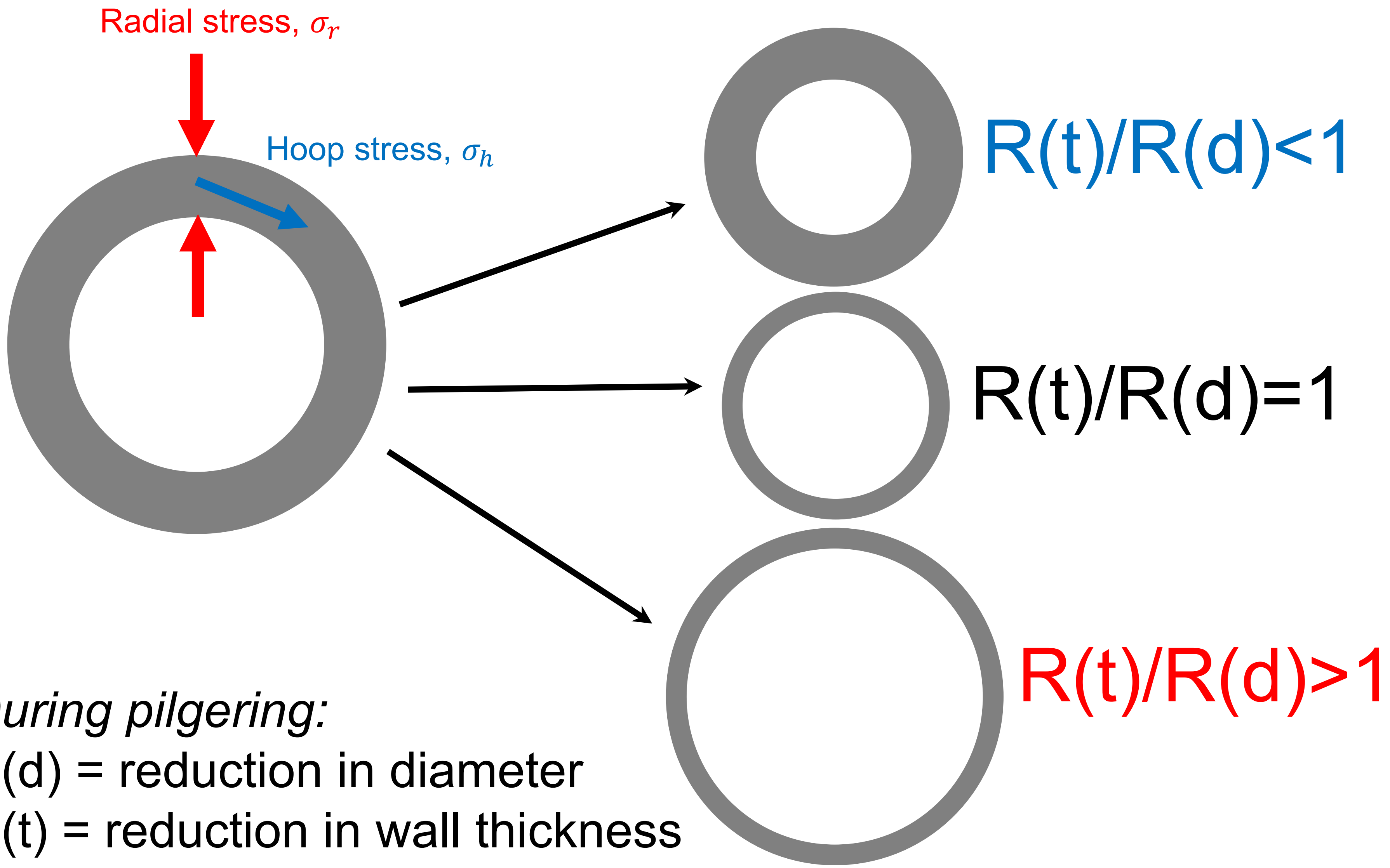


A schematic of hcp texture formation in a Zr cladding tube.

Texture Development during Pilgering

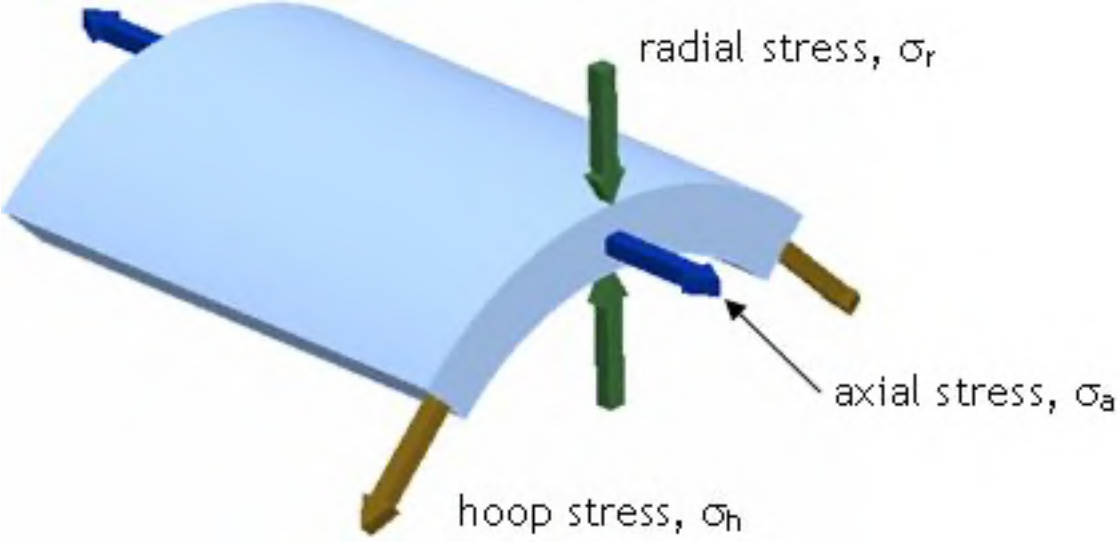
- Allows independent reduction of wall thickness and diameter, to control final shape of the cladding rods.
- *Note, change in stress state of material for different regimes.*

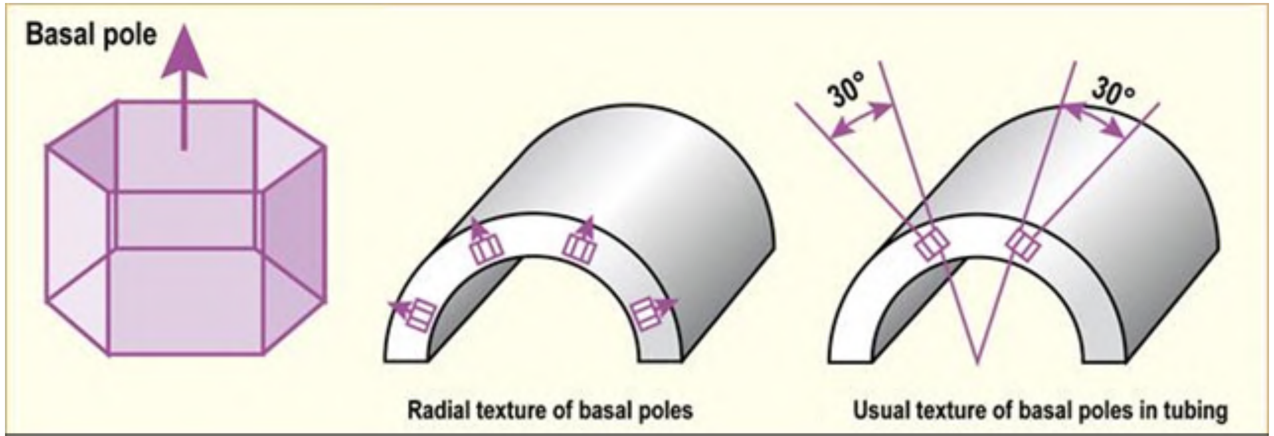


During pilgering:
R(d) = reduction in diameter
R(t) = reduction in wall thickness

Texture Development during Pilgering

- During deformation, the basal poles align with the major compressive stresses.
- Related to slip and twinning in α-phase during deformation.





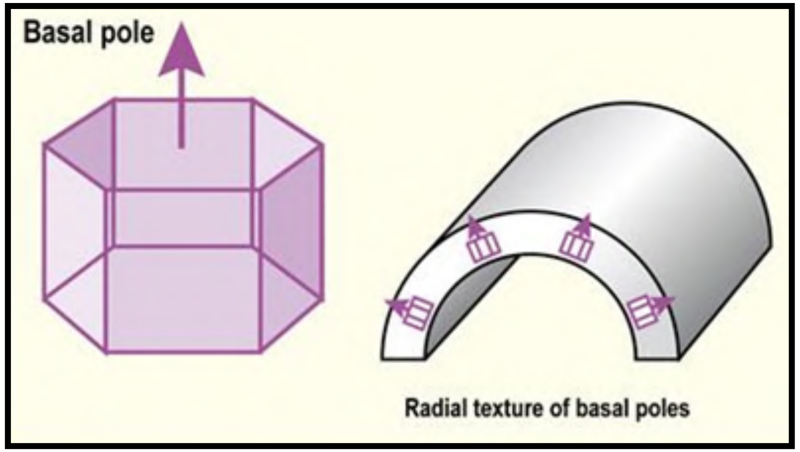
Basal pole orientation in cladding and pressure tubing.[1]

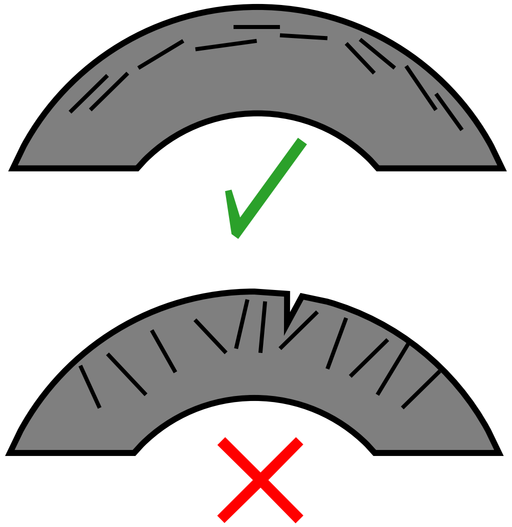
- When R(t)/R(d) < 1 → c-axis orientated along tangential (hoop) direction
- When R(t)/R(d) > 1 → c-axis orientates along radial direction ***(radial texture)***

Effect of Texture in *Cladding Material (Advantage)*

1. Hydrides

- Precipitate on basal plane
- Alignment in radial direction less detrimental

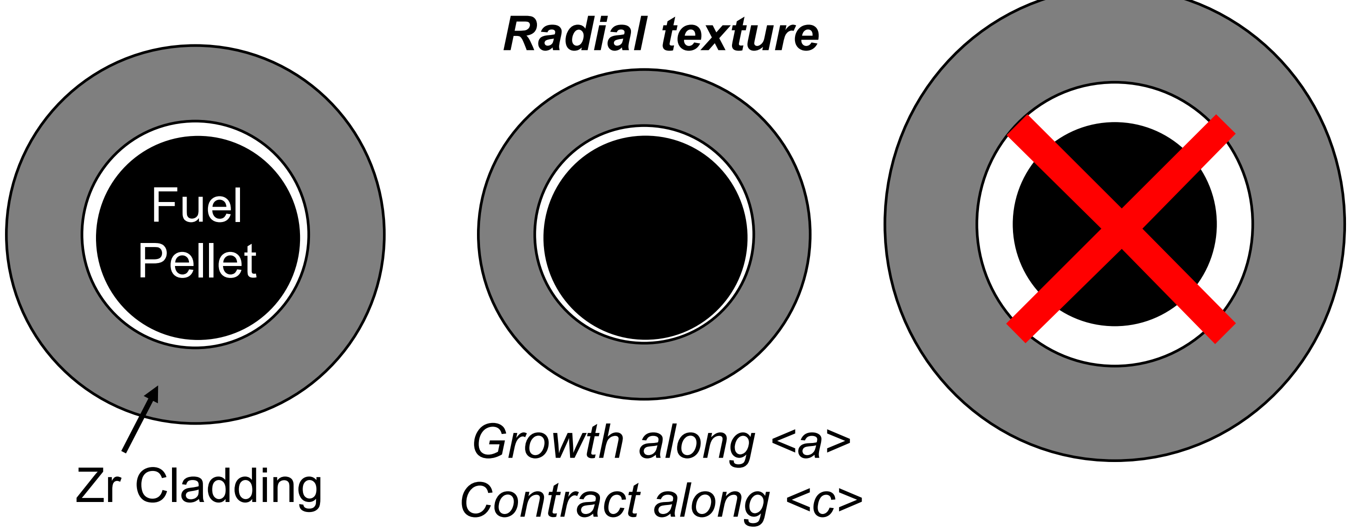




Hydrides in Zr alloy tube.

2. Irradiation growth

- Reduce gap between fuel pellet and cladding *(would act as thermal barrier)*



Effect of Texture for *Cladding Material (Disadvantage)*

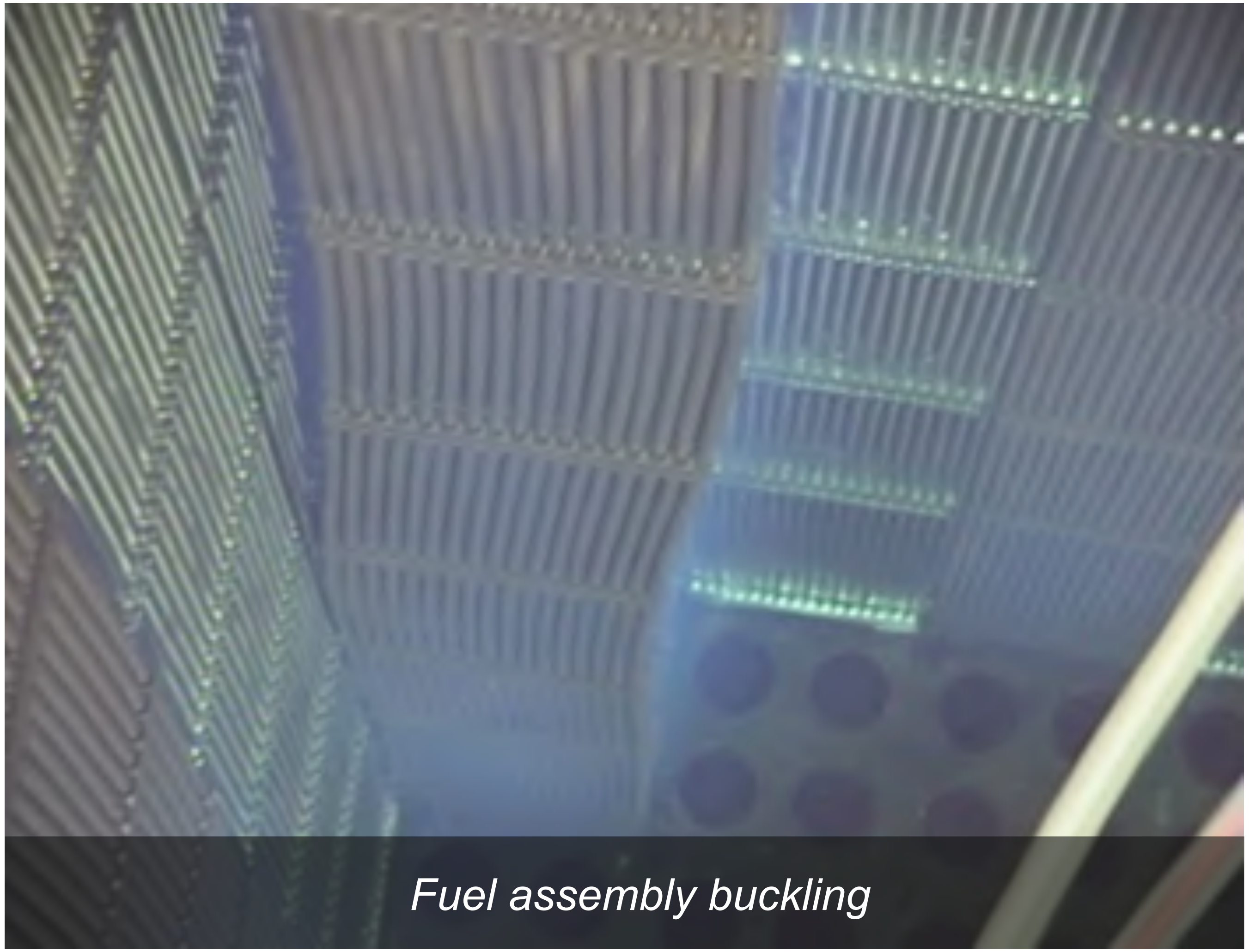
Irradiation growth

- *Growth along <a> direction.*
- *Contraction along <c> direction*

- Accelerated irradiation growth can leads to elongation of the fuel assembly.

- High elongation → buckling.

- Growth along axial direction controlled by texture in channel structures…

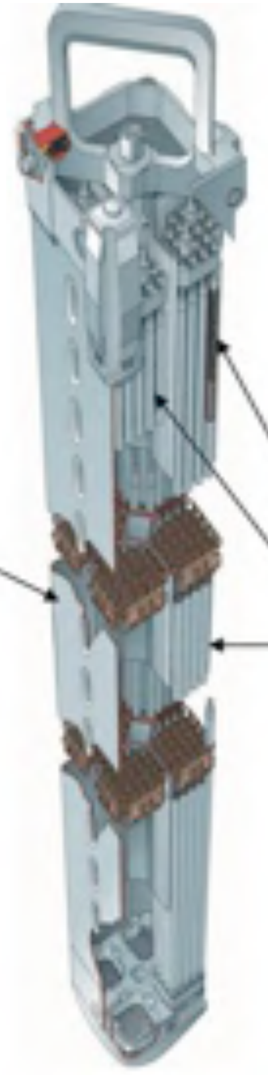


Fuel assembly buckling

Effect of Texture for *Channel Structures (Disadvantage)*

- Zr alloys also used as material for fuel channel in BWRs (to direct coolant flow).
- Sheets connected to ends of fuel assembly, so sensitive to irradiation growth.
- Irradiation gradient → channel bowing and buckling.

BWR
Boiling Water Reactor



Boiling water at
274 – 288°C
with
pH 5.6, 50ppb H_2

Randomising Texture in *Channel Structures*

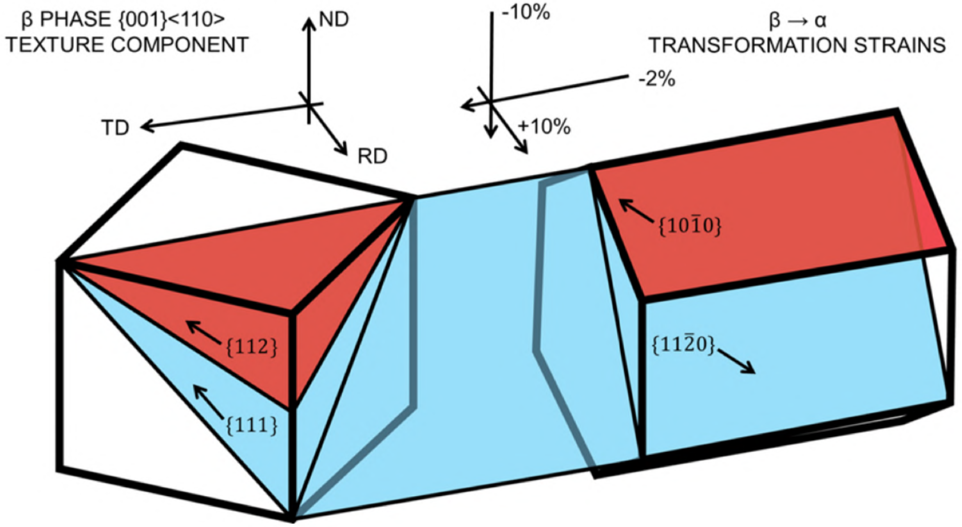
- β-quench material after thermomechanical processing

- α → β transformation on heating (6 possible β variants)

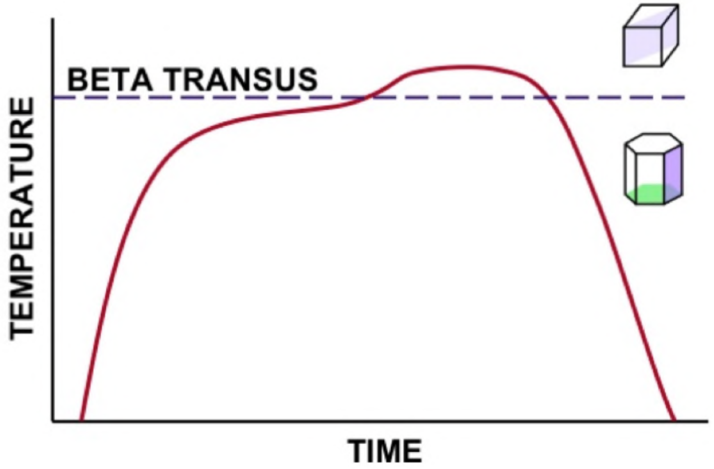
- β → α transformation on cooling (12 possible α variants)

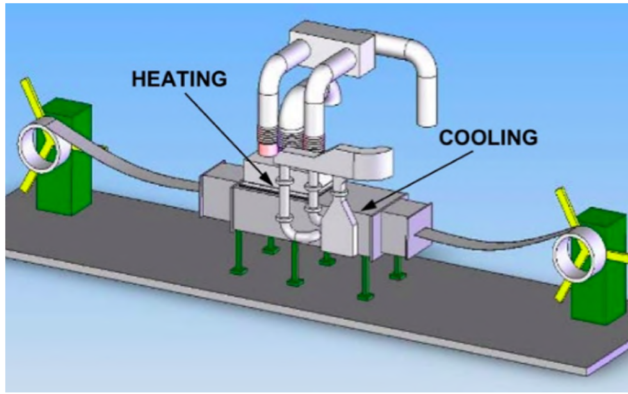
↓

- 72 possible α variants after β-quenching!



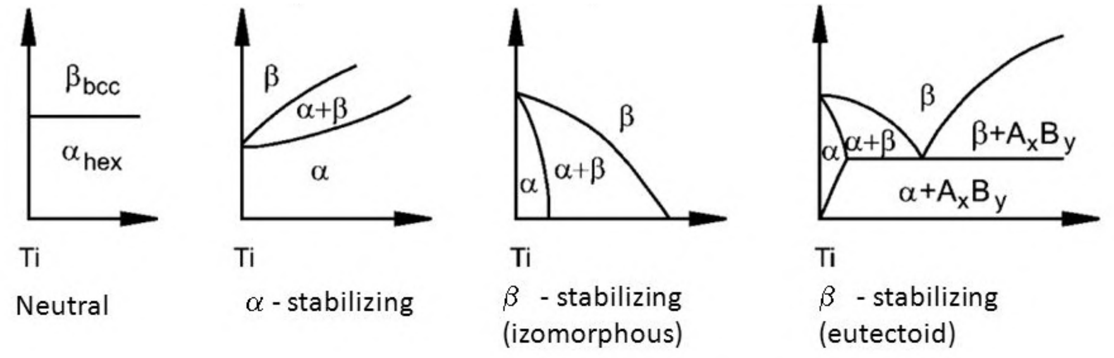
$\{110\}_{\beta} \parallel (0002)_{\alpha}$ and $\langle 111 \rangle_{\beta} \parallel [1120]_{\alpha}$





Second Phase Particles (SPPs) in Zr Alloys

- Eutectoid alloying elements have a very low solubility in the metal matrix.



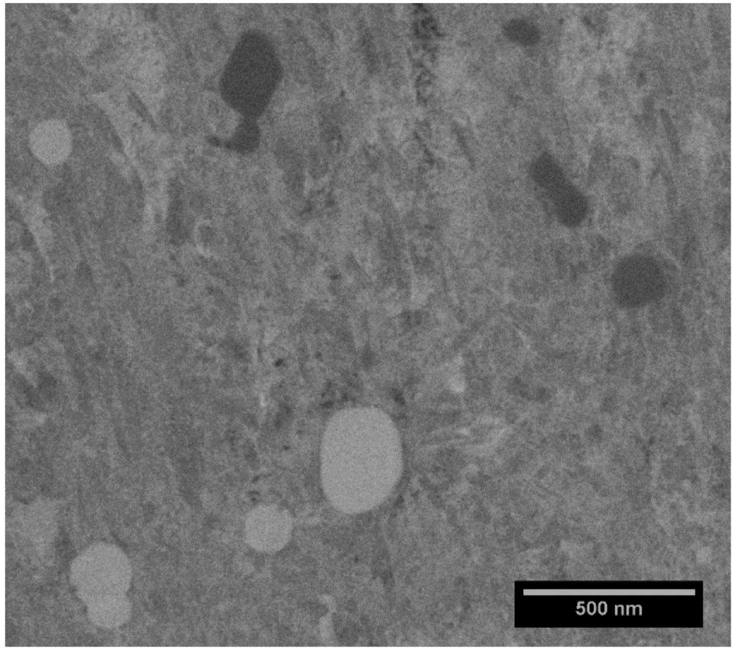
α-stabilising increase β-transus
β-stabilising decrease β-transus
Isomorphous – completely soluble in solid solution
Eutectoid – intermetallic particles are created

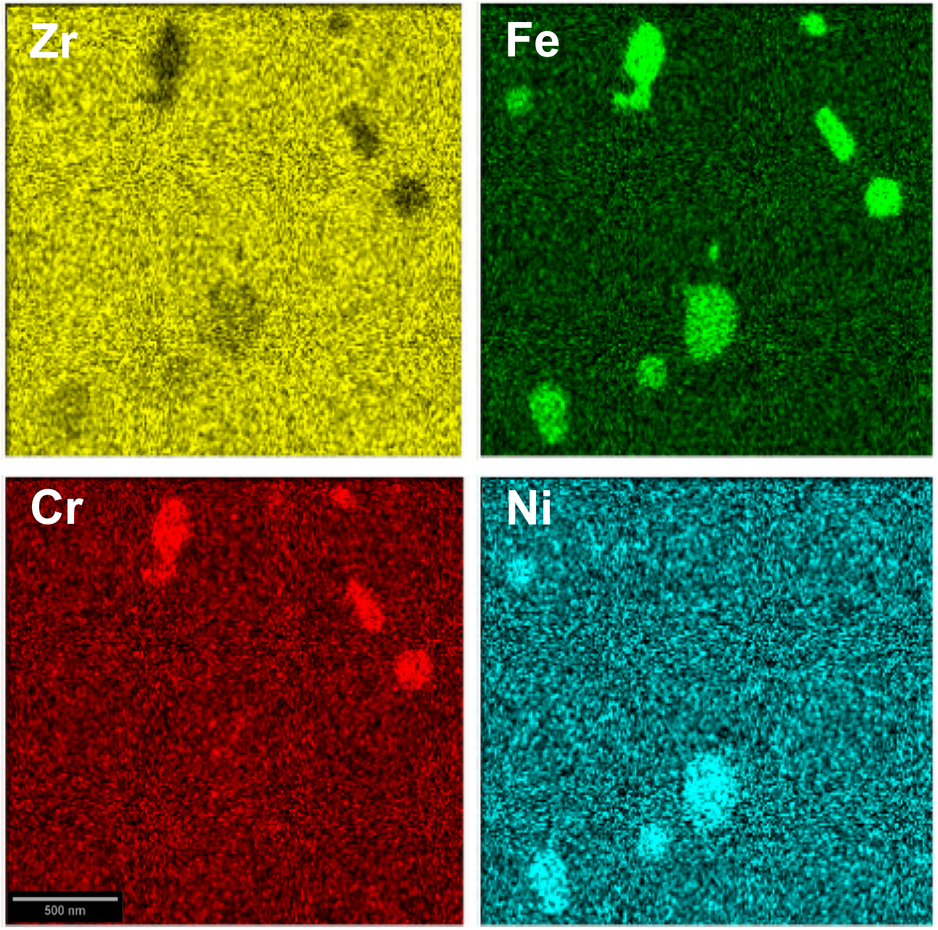
- In Zr-alloys, solubility of Fe, Cr, Ni is almost zero.
- Fe and Nb are eutectoid elements. Fe is always present in Zr-alloys (very difficult to eliminate) and ***was*** often added as an alloying element.
- Annealing temperature and time has great effect on size of SPPs.
- SPP size seems to affect corrosion performance but mechanisms unclear.

Second Phase Particles (SPPs) in Zr Alloys

- SEM images and EDX maps of a Zr-alloy (HIFI) ***after pilgering and annealing.***

- SPPs mainly ***intragranular*** *(within the grains).*





Second Phase Particles (SPPs) in Zr Alloys

- STEM images and EDX maps of a Zr-alloy (HIFI) ***after β-quenching.***
- SPPs now mainly ***intergranular*** *(at grain boundaries).*
- *How does this affect the in-reactor behaviour?*