Agency for Innovation by Science & Technology

MatISSE/JPNM Workshop on Cross-Cutting Issues in Structural Materials R&D for Future Energy Systems

Exploring the Potential of MAX Phases for Select Applications in Extreme Environments

K. Lambrinou[1], T. Lapauw[1,2], J. Vleugels[2]

[1] SMR Group, NMS Institute, SCK•CEN; [2] Dept. MTM, KU Leuven

in collaboration with Sandvik, KIT, MPIE, U Poitiers, Linköping U, Drexel U

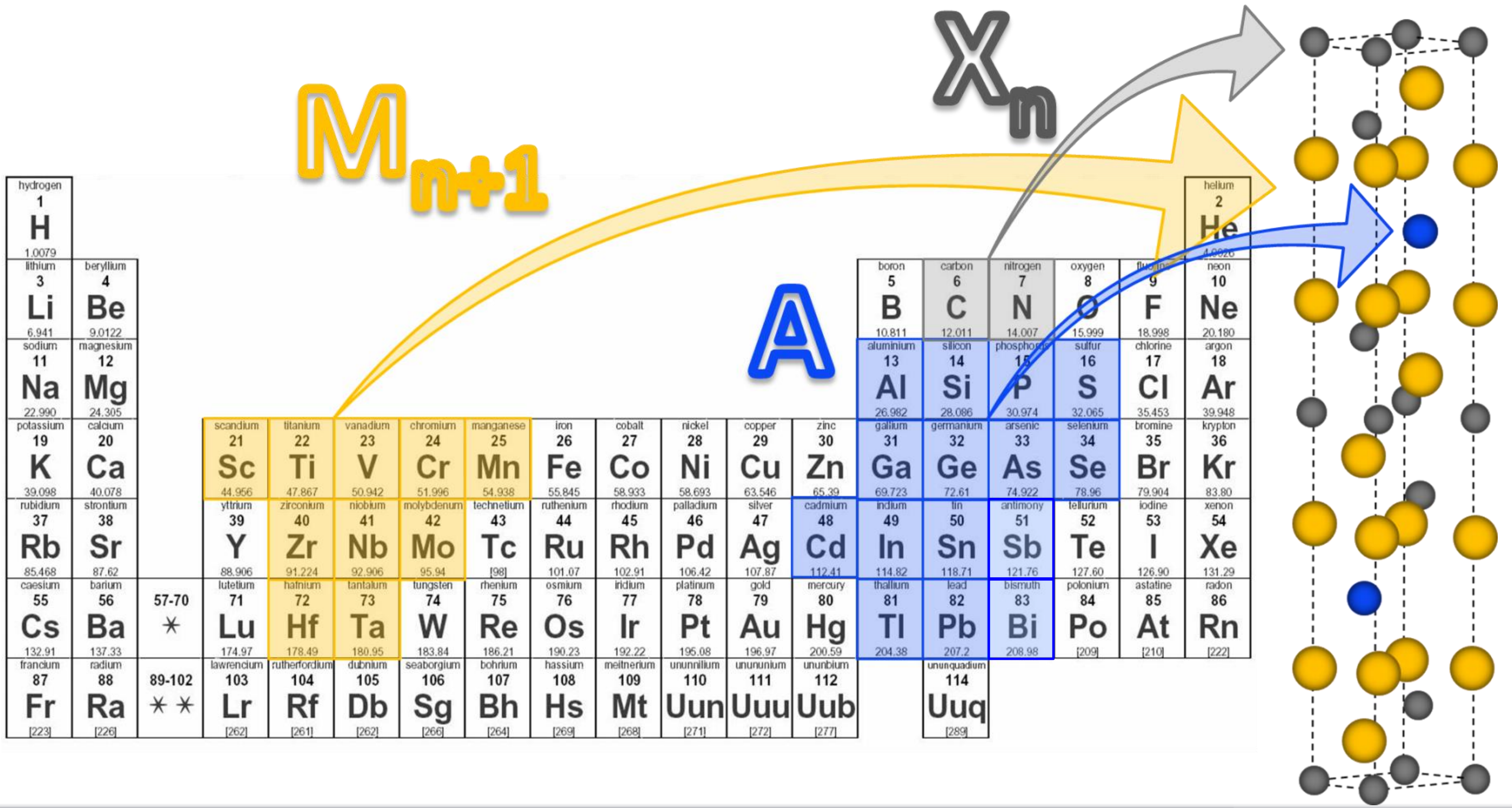
JRC-IET, Petten, The Netherlands, 26/11/2015

Outline

- General Introduction
  - Why MAX Phases?
  - MAX Phases for Advanced Nuclear Systems
- MAX Phases for Gen-IV LFRs: MYRRHA Pump Impeller
  - Nb-Al-C System: Nb_4AlC_3
  - Nb-Zr-Al-C System: $(Nb,Zr)_4AlC_3$
  - Processing towards Mechanical Property Optimization
  - Resistance to Dissolution Corrosion in LBE
  - Resistance to Flow-Assisted Corrosion in LBE
- MAX Phases for Gen-III+ LWRs: Accident-Tolerant Fuels (ATFs)
  - Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC
- Conclusions

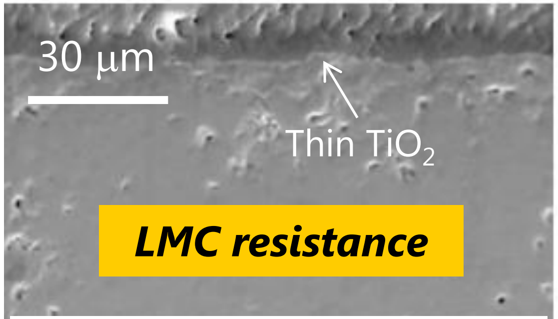
MAX Phases: Introduction

- MAX phases: ternary carbide and nitride compounds described by the general formula $M_{n+1}AX_n$, where n = 1, 2, 3
- Laminated crystal structure: **M_6X** octahedra interleaved with **A** layers



MAX Phases: Why?

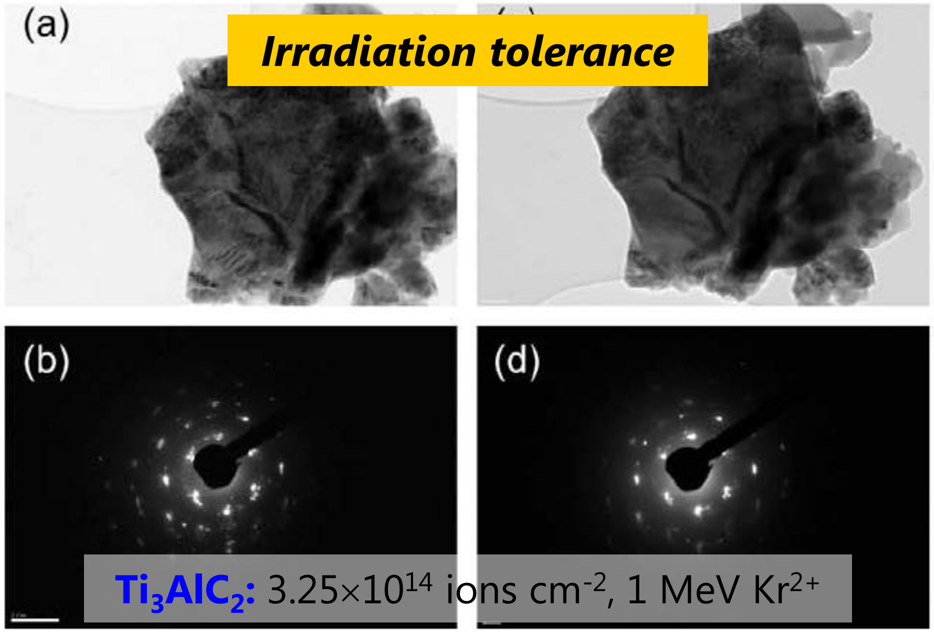
- Unique combination of physical, chemical, mechanical properties, e.g. LMC resistance, machinability, damage tolerance, irradiation tolerance, …

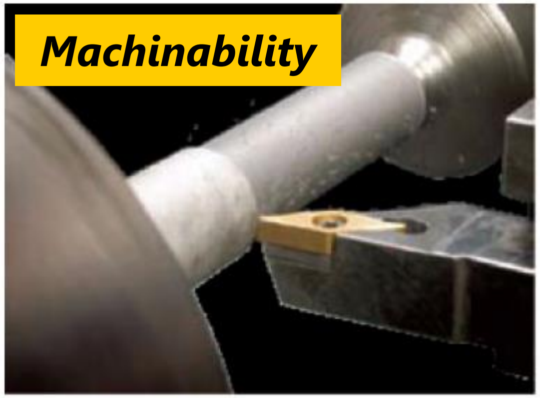


Ti_3SiC_2: 650°C, 3000 h, [O] ≈ 10^{-8} mass%, static LBE

*(A. Heinzel et al., Journal of Nuclear Materials **392** (2009) 255-258)*

*(M.W. Barsoum & M. Radovic, Annu. Rev. Mater. Res. **41** (2011) 195-227)*

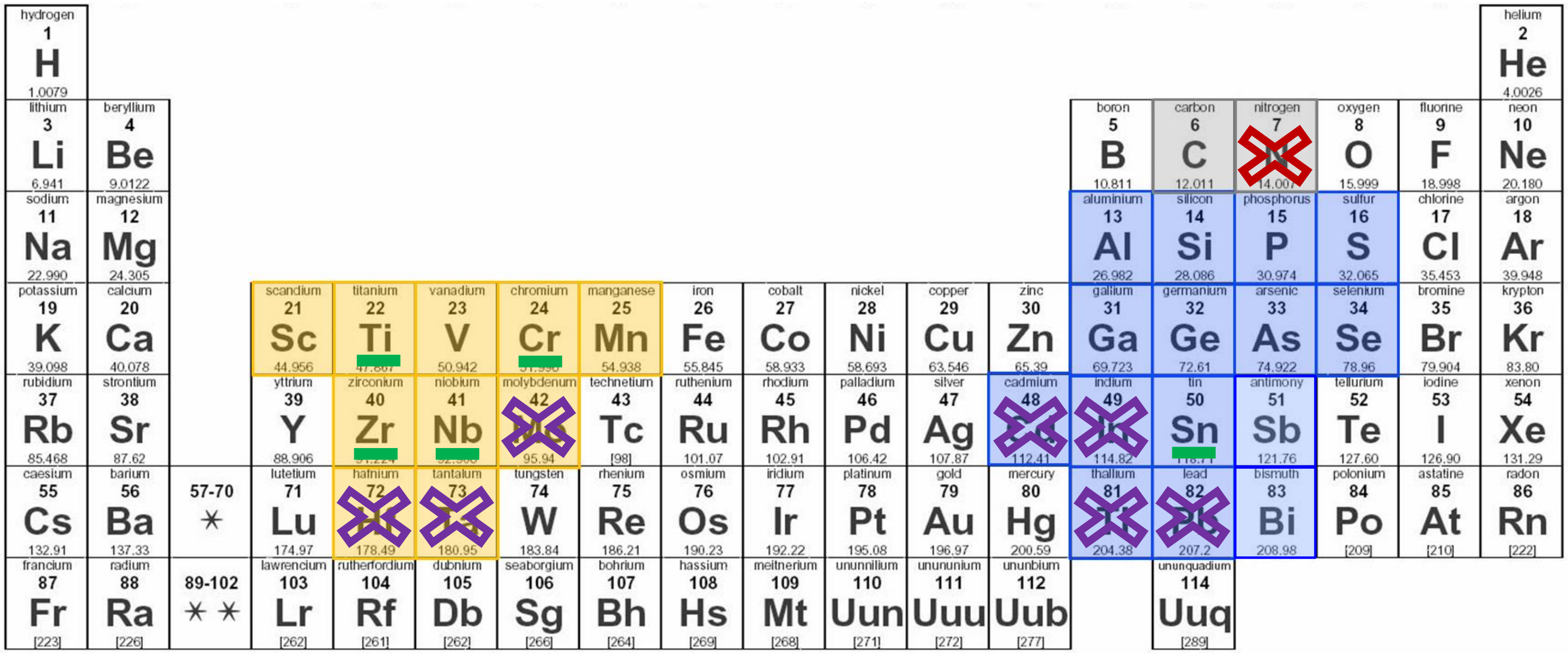




*(M.W. Barsoum & M. Radovic, Annu. Rev. Mater. Res. **41** (2011) 195-227)*

*(K.R. Whittle et al., Acta Materialia **58** (2010) 4362-4368)*

MAX Phases for Advanced Nuclear Systems

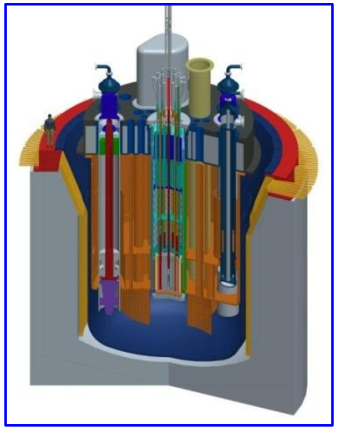


- Large neutron cross-section
- Long-lived isotope ^{14}C
- Alloying elements in commercial clads (Zircaloy/ZIRLO/15-15Ti SS)

➢ Systems of interest: **Nb-Al-C, Zr-Al-C** and **solid solutions thereof**

Outline

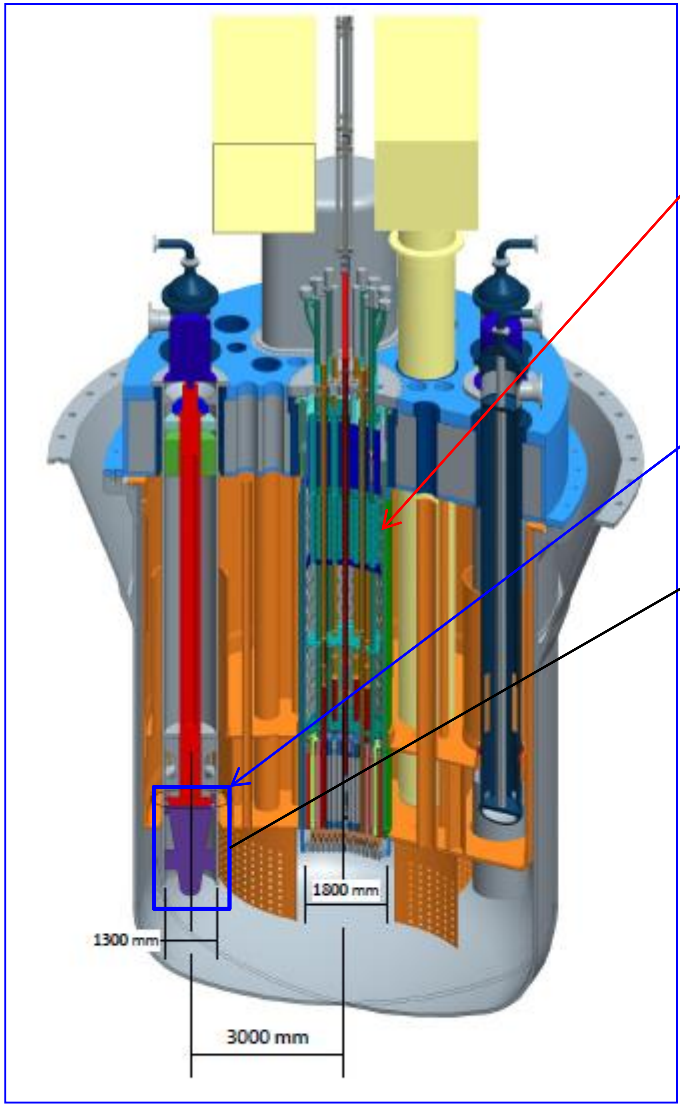
- General Introduction
  - Why MAX Phases?
  - MAX Phases for Advanced Nuclear Systems
- MAX Phases for Gen-IV LFRs: MYRRHA Pump Impeller
  - Nb-Al-C System: Nb_4AlC_3
  - Nb-Zr-Al-C System: $(Nb,Zr)_4AlC_3$
  - Processing towards Mechanical Property Optimization
  - Resistance to Dissolution Corrosion in LBE
  - Resistance to Flow-Assisted Corrosion in LBE
- MAX Phases for Gen-III+ LWRs: Accident-Tolerant Fuels (ATFs)
  - Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC
- Conclusions



MAX Phases for Gen-IV LFRs: MYRRHA Pump Impeller

SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

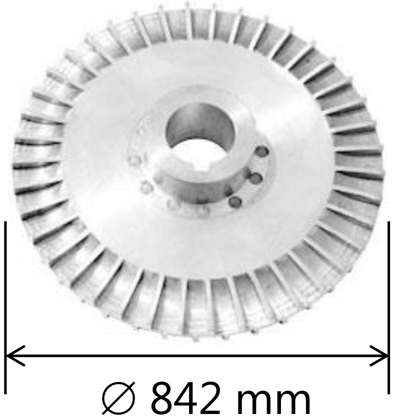
MYRRHA: Pump Impeller Application



Maximum allowable dose at core barrel:
2 dpa

Pump Impeller
(< 1 dpa)

Pump Impeller Rotor*

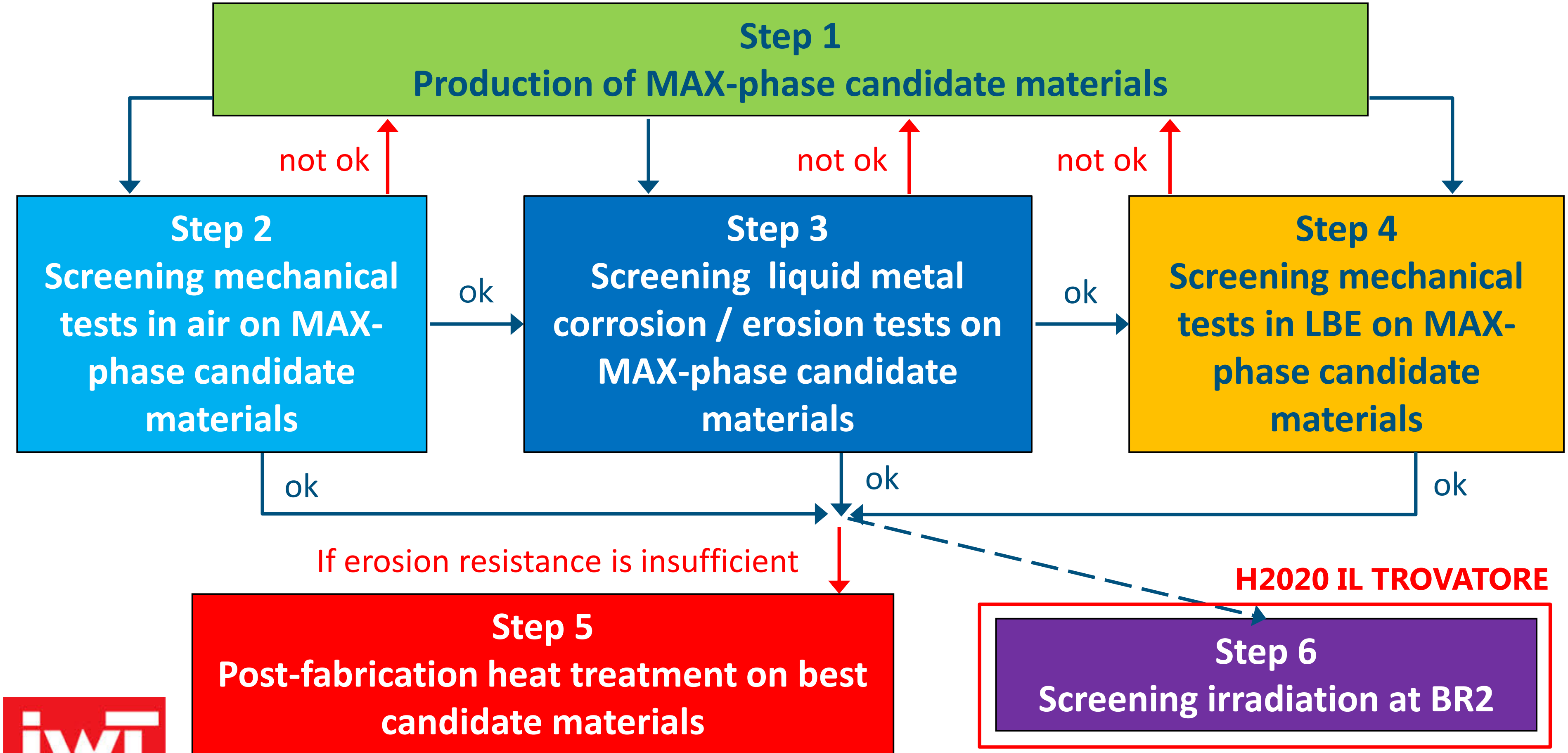


- MYRRHA Pump Impeller Service Conditions:
  - $T_{max} \approx 270°C$ ($T_{max} \approx 480°C$ in Gen-IV LFRs)
  - LBE flow velocity: $v \approx$ 10-20 m/s locally
  - Dissolved oxygen in LBE: [O] $\approx 10^{-6}$ mass%
  - Fast neutron irradiation dose: low (< 1 dpa)
  - Other targeted property requirements (strength, fracture toughness, fatigue resistance)

❖ Not latest MYRRHA design!

* Not actual MYRRHA pump impeller design!

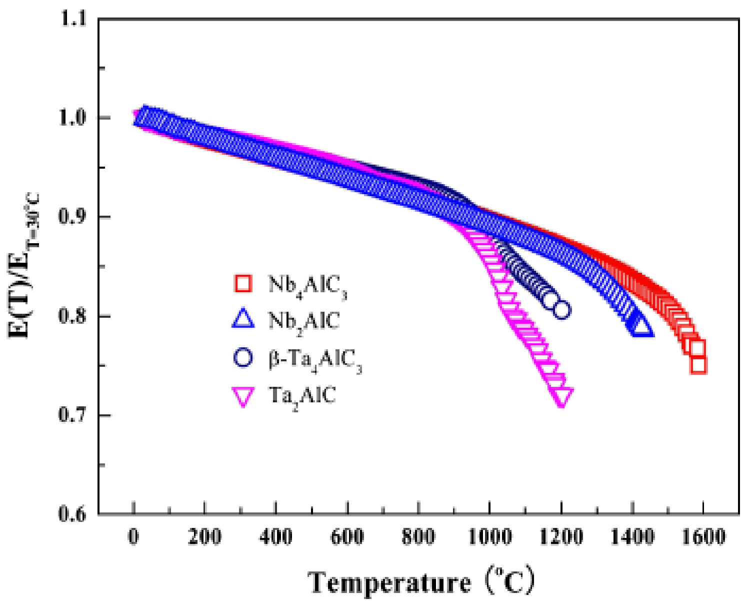
MYRRHA Pump Impeller: R&D Approach



Nb-Al-C System: Nb_4AlC_3

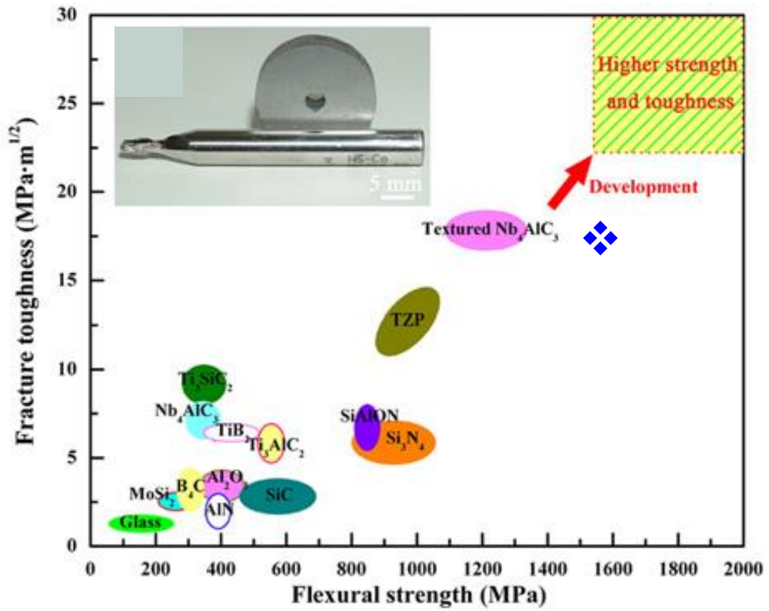
- Nb_4AlC_3 shows great potential as high-T structural material due to:
  - Good thermal stability as reflected in high-T mechanical properties
  - High fracture toughness (7.1 MPa·m$^{1/2}$ untextured; 17.9 MPa·m$^{1/2}$ textured)

Normalized Young's Modulus

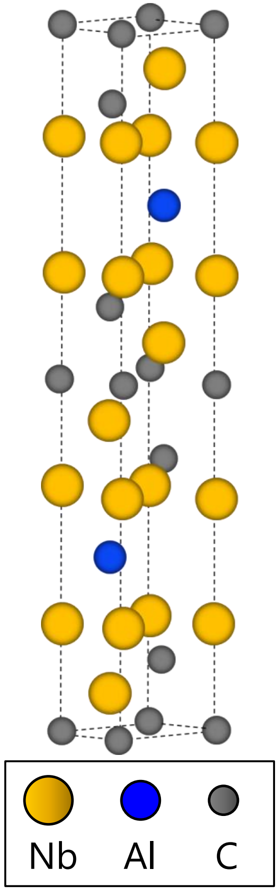


*(C.F. Hu et al., Journal American Ceramic Society **91** (2008) 2258-2263)*

Fracture Toughness



*(C.F. Hu et al., Scripta Materialia **64** (2011) 765–768)*



❖ Slip casting in magnetic field (12 T) & SPS

KU LEUVEN

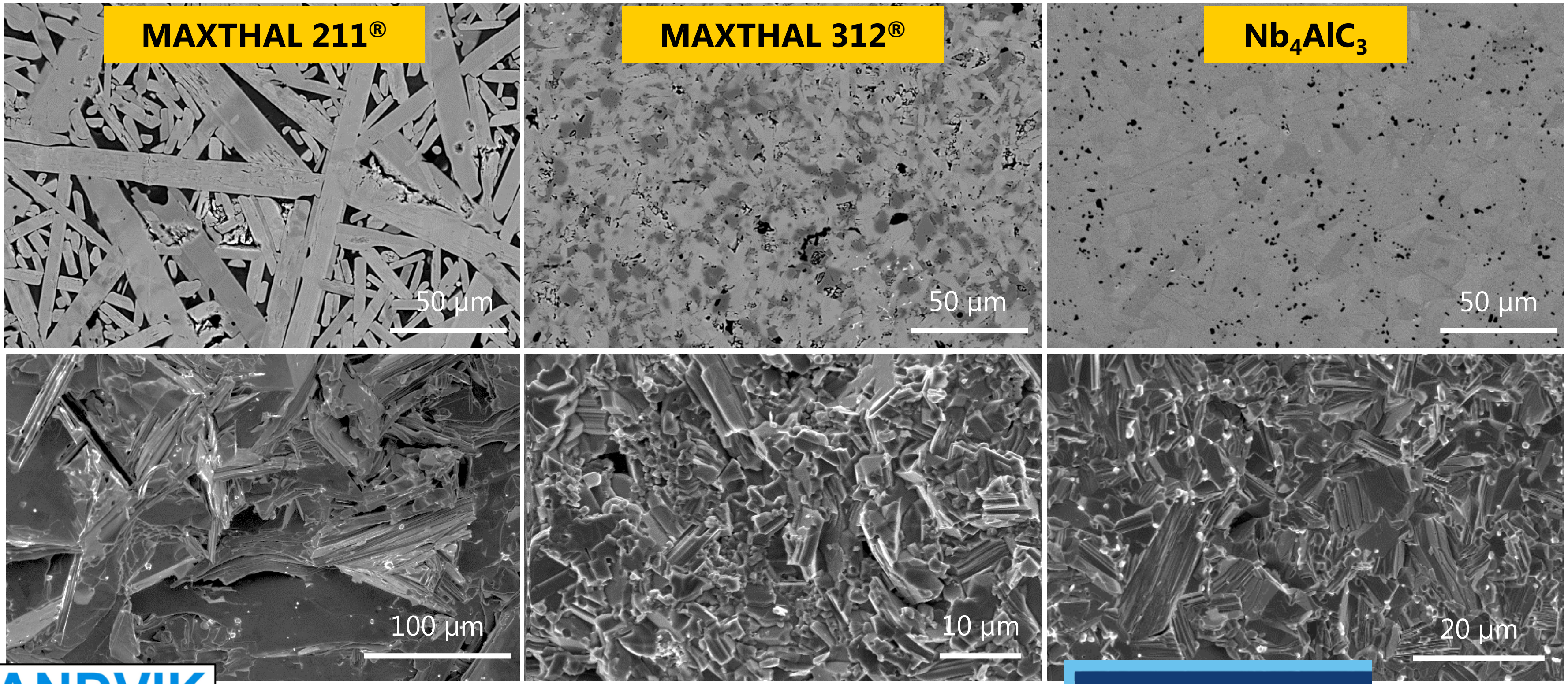
Nb-Al-C System: Nb_4AlC_3

Iterative Optimization

Starting Powders	Nb powder + Al powder + Carbon black
Preparing Stoichiometry	Ratio Nb : Al : C = 4 : 1-1.5 : 2.3-3
Mixing Powders	Wet/Dry Turbula Mixing Wet/Dry Planetary Ball Milling
Cold Pressing	Graphite die Pressure: 30 MPa
Pressure-Assisted Sintering	Graphite die Vacuum HP/SPS Temperature range: 1600-1900°C Pressure: 0-50 MPa
Characterisation: LOM / SEM / XRD	

Comparison of MAXTHAL 211® & 312® to Nb_4AlC_3

- Commercially-available MAXTHAL 211® (nominally Ti_2AlC) & MAXTHAL 312® (nominally Ti_3SiC_2) were provided by SANDVIK*
- Nearly single-phase Nb_4AlC_3 was produced by SPS (1650°C) at KU Leuven
- All 3 materials were characterized in terms of microstructure & properties



SANDVIK

(*Courtesy: E. Ström)

KU LEUVEN

Comparison of MAXTHAL 211® & 312® to Nb_4AlC_3

Property	MAXTHAL 211®	MAXTHAL 312®	Nb_4AlC_3
Composition (wt%)	55 Ti_2AlC + 38 Ti_3AlC_2 + 7 $TiAl_3$	90 Ti_3SiC_2 + 10 TiC	98 Nb_4AlC_3 + 2 Al_2O_3
ρ (g/cm^3)	4.02 (98% ρ_{th})	4.42 (98% ρ_{th})	6.89 (99% ρ_{th})
Grain size (µm)	50-100	5-10	10-20
E (GPa)	265 ± 4	325 ± 5	340 ± 5
G (GPa)	112 ± 2	137 ± 3	137 ± 2
ν	0.17	0.19	0.23
T (°C) where E/E_{RT}* = 0.75	± 1250	± 1300	> 1400
$H_{V,3kg}$ (GPa)	3.2 ± 0.5	3.8 ± 0.4	3.7 ± 0.3
σ_{4PB} (MPa)	210 ± 12	404 ± 44	573 ± 39
K_{IC} (MPa·m$^{1/2}$)	6.2 ± 0.2	4.8 ± 0.2	6.6 ± 0.1

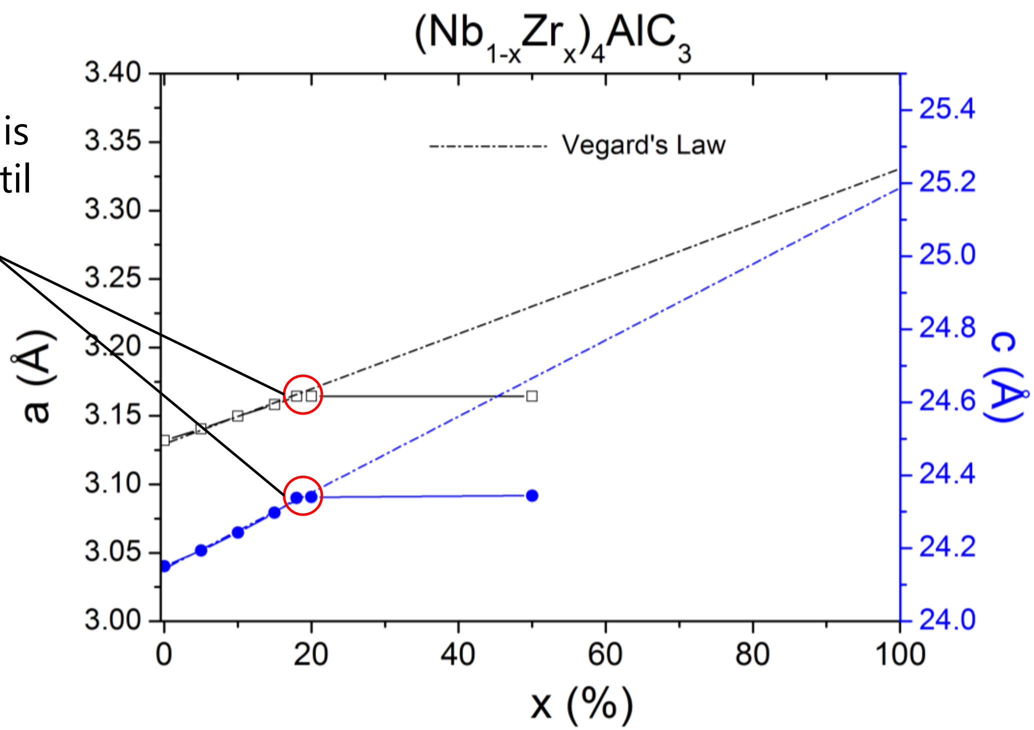
* High-T E measured in vacuum

KU LEUVEN

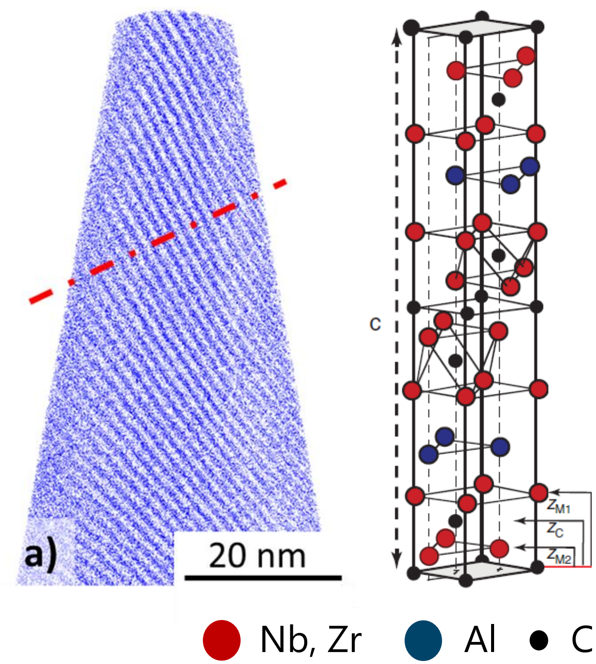
Nb-Zr-Al-C System: $(Nb,Zr)_4AlC_3$ solid solution

- Substituting Nb with Zr in Nb_4AlC_3 lattice could have beneficial effect on:
  - Smaller neutron cross-section than Nb_4AlC_3 ✓
  - Mechanical properties **?**
  - Temperature stability **?**
- Maximum Zr solid solubility in $(Nb_{1-x}Zr_x)_4AlC_3$:
  - x ≈ 18%; further Zr increase forms ZrC

Vegard's law is respected until x ≈ 18%



Atom Probe Tomography

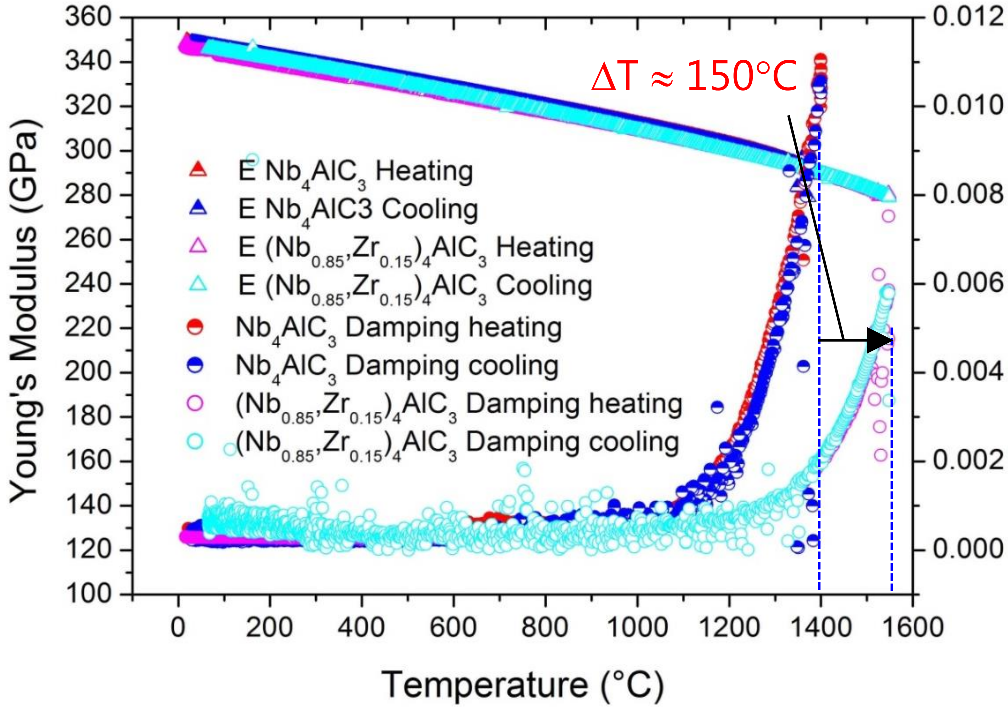


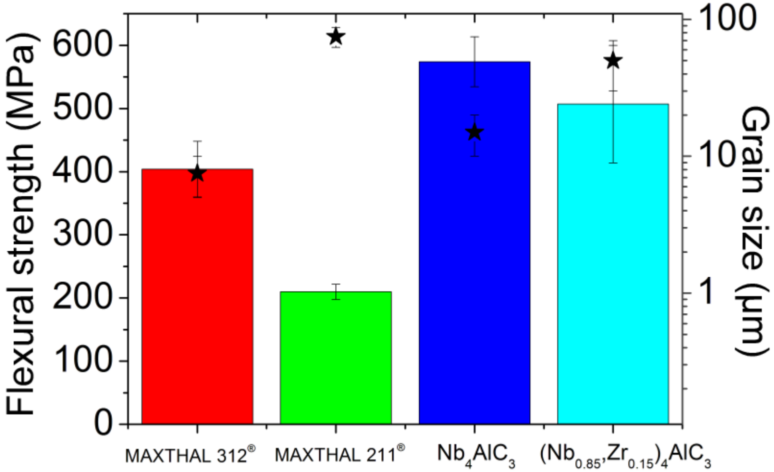
Max-Planck-Institut für Eisenforschung GmbH

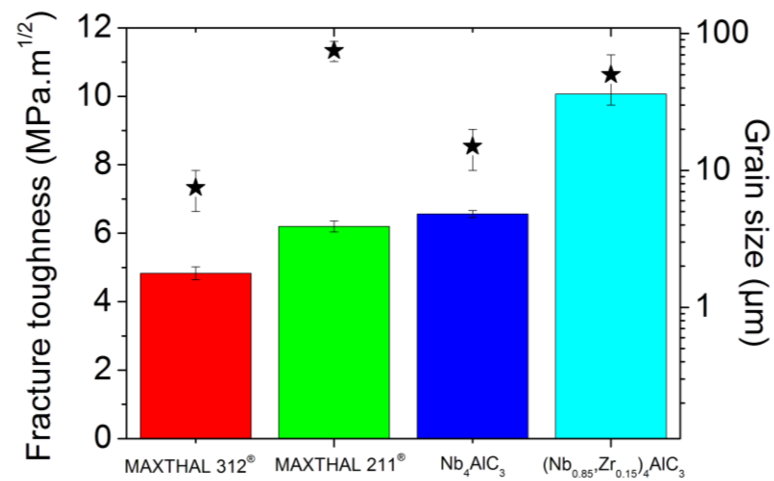
(*Courtesy:* *D. Tytko, P. Choi, D. Raabe*)

Nb-Zr-Al-C System: Nb_4AlC_3 & $(Nb,Zr)_4AlC_3$

- Substituting Nb with Zr in Nb_4AlC_3 has beneficial effect on:
  - Smaller neutron cross-section than Nb_4AlC_3 ✓
  - Mechanical properties ✓
  - Temperature stability ✓



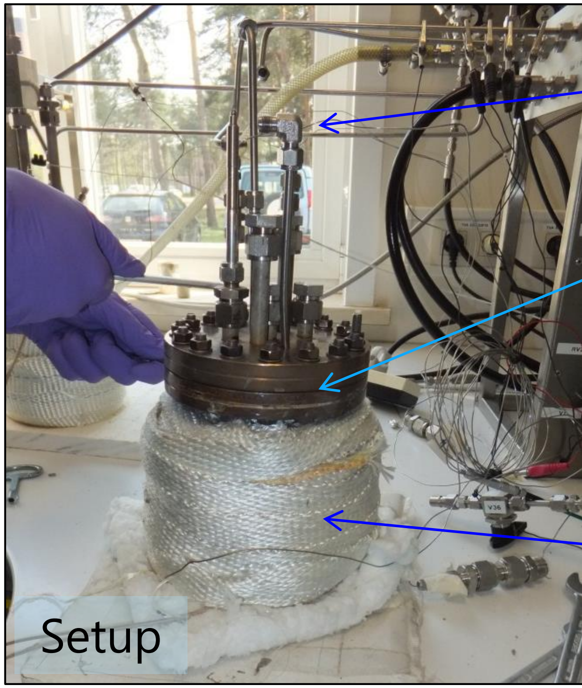




KU LEUVEN

SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Resistance to Dissolution Corrosion: Test Setup



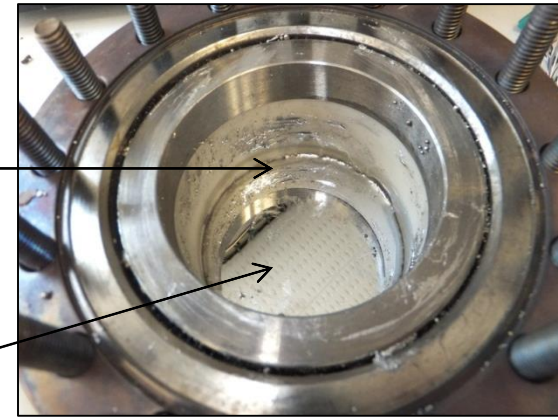
Pipes for gas inlet/outlet

Steel container

Thermal insulation

Al_2O_3 inner liner

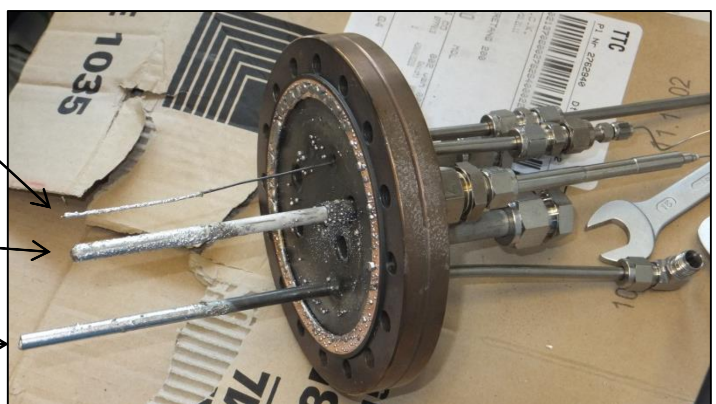
Cleaned LBE surface



Thermocouple

Oxygen sensor (Bi/Bi_2O_3)

Gas inlet pipe



Graphite plate

Mo wires

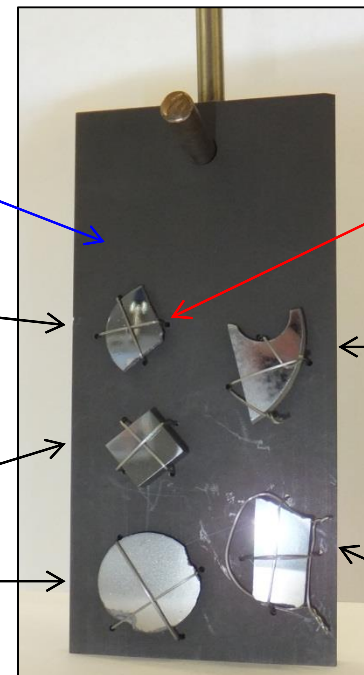
Nb_2AlC

MAXTHAL 211®

Ti_3AlC_2

MAXTHAL 211® (SANDVIK powder)

MAXTHAL 312®

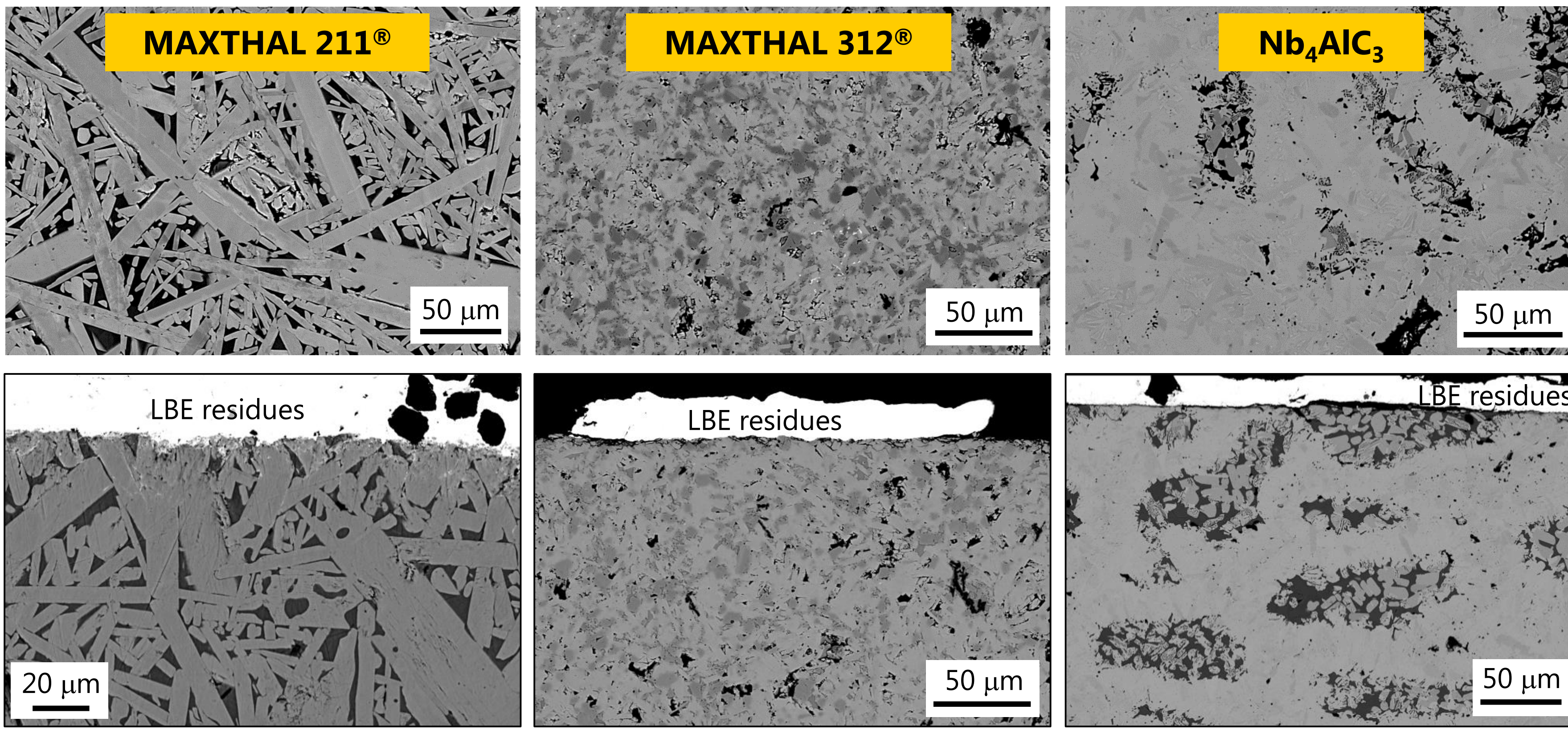


LMC Test Results – SEM Data

- Materials: MAXTHAL 211® & MAXTHAL 312® provided by SANDVIK; various MAX phases and early-grade Nb_4AlC_3 produced by SPS (KU Leuven)
- Test: 3501 h, 500°C, [O] ≈ $10^{-14} \div 10^{-10}$ mass%, static LBE
- **No sign of LBE dissolution attack** was found on the exposed MAX phases

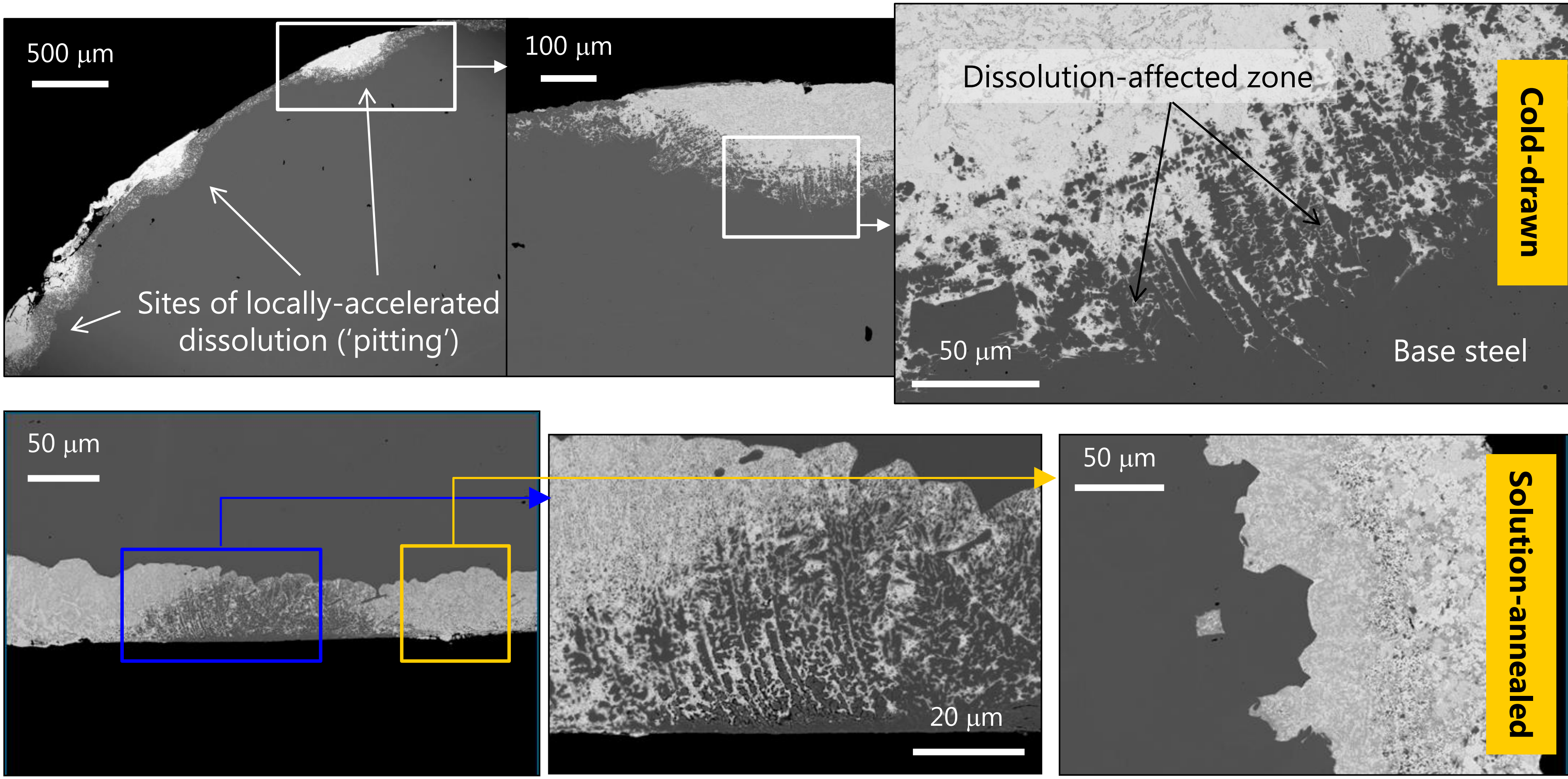
Pristine Materials

Exposed Materials



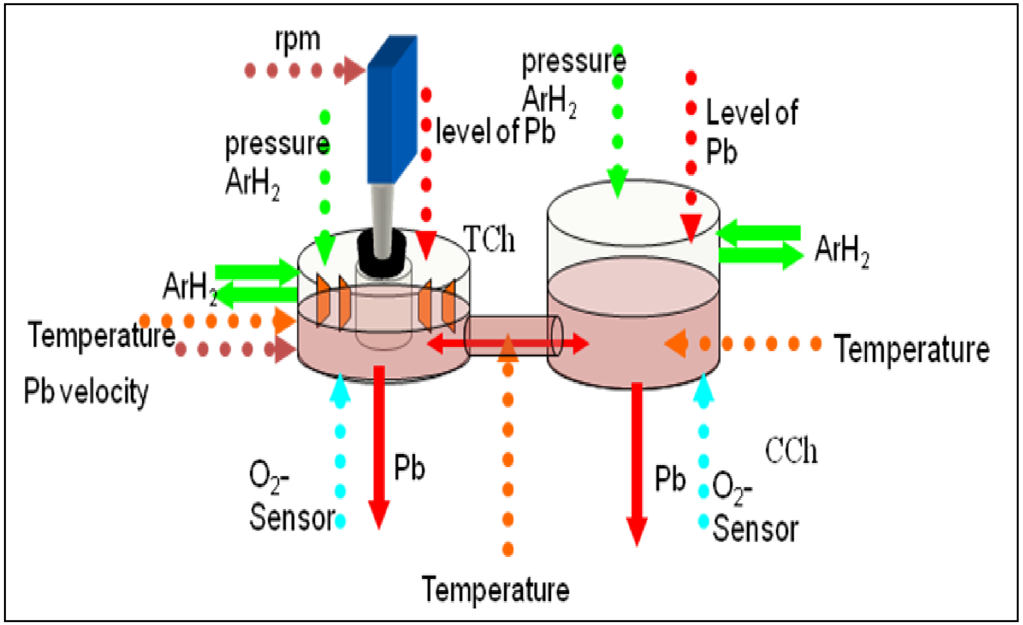
LMC Behavior of MAX Phases vs. 316L SS

- LMC Test Summary: 3282 h, 500°C, [O] ≈ $8\times10^{-13}\div3\times10^{-8}$ mass%, static LBE
- Dissolution zone: 9-152 μm solution-annealed steel; 50-348 μm cold-drawn steel

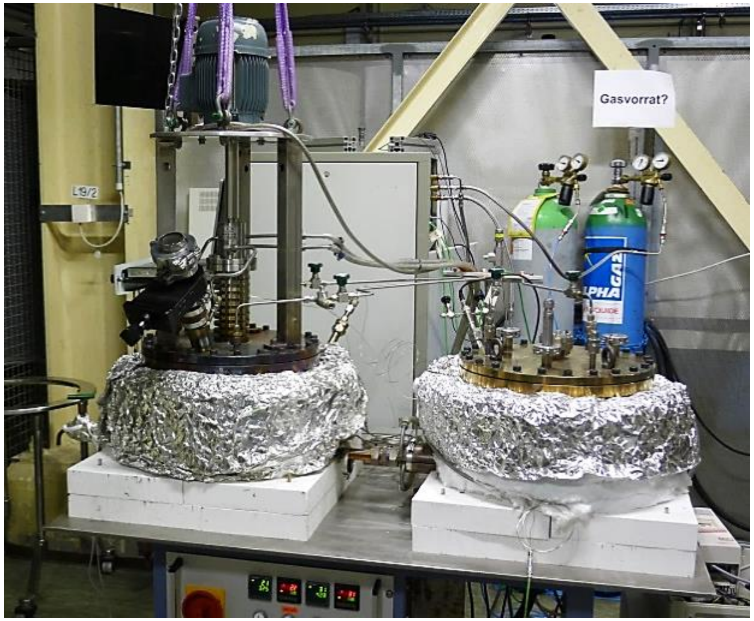


Resistance to Flow-Assisted Corrosion: Test Setup

- Test Setup: CORELLA (CORrosion Erosion facility for Liquid Lead Alloy) Facility, KIT, Germany –
  - Material testing in contact with fast-flowing Pb/LBE (>1000 rpm and Pb/LBE flow velocities v > 10 m/s)
  - Monitoring of T and [O] (Bi/Bi_2O_3 ref. electrode) during testing
  - Testing at [O] constant by conditioning Pb/LBE with appropriate gas mixtures



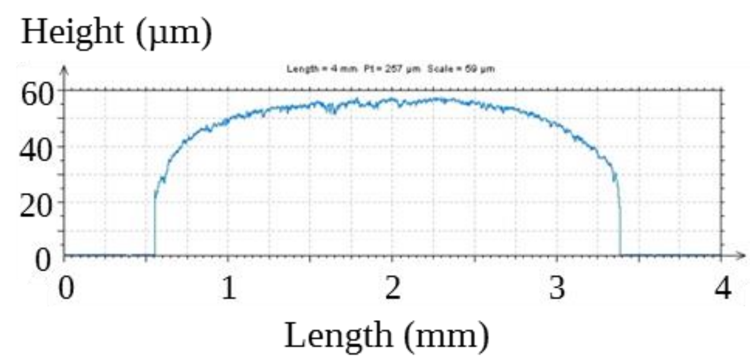
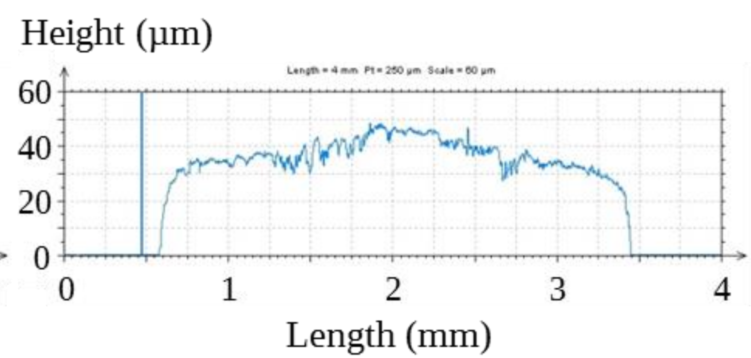
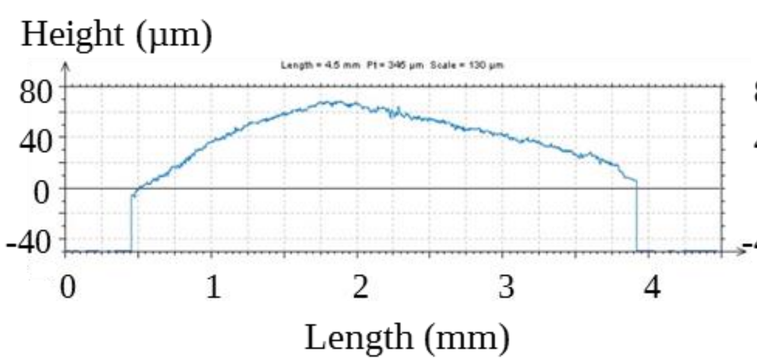
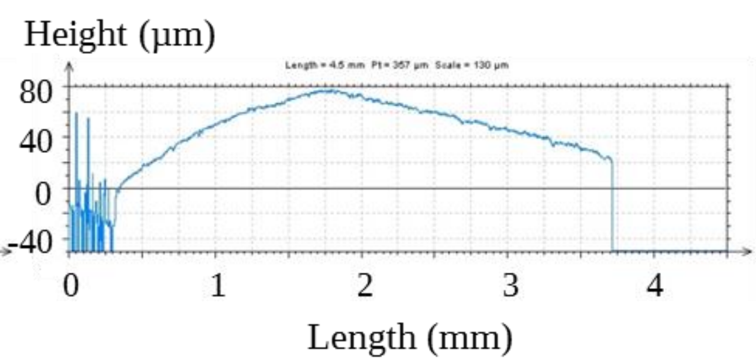
TCh: test chamber; CCh: conditioning chamber



Samples: 60×15×1.5 mm^3

CORELLA Test Results

- White light interferometry was used to assess damages on commercial Maxthal® materials: **no signs of flow-assisted corrosion (erosion) damage!**
- Screening tests: 500/500/1000 h, 300°C, liquid LBE, [O] ≈ 10^{-6} mass%, v ≈ 8 m/s
- Surface profilometry results on tested MAX materials:

	Pristine Materials	Exposed Materials
MAXTHAL 211®		
MAXTHAL 312®		

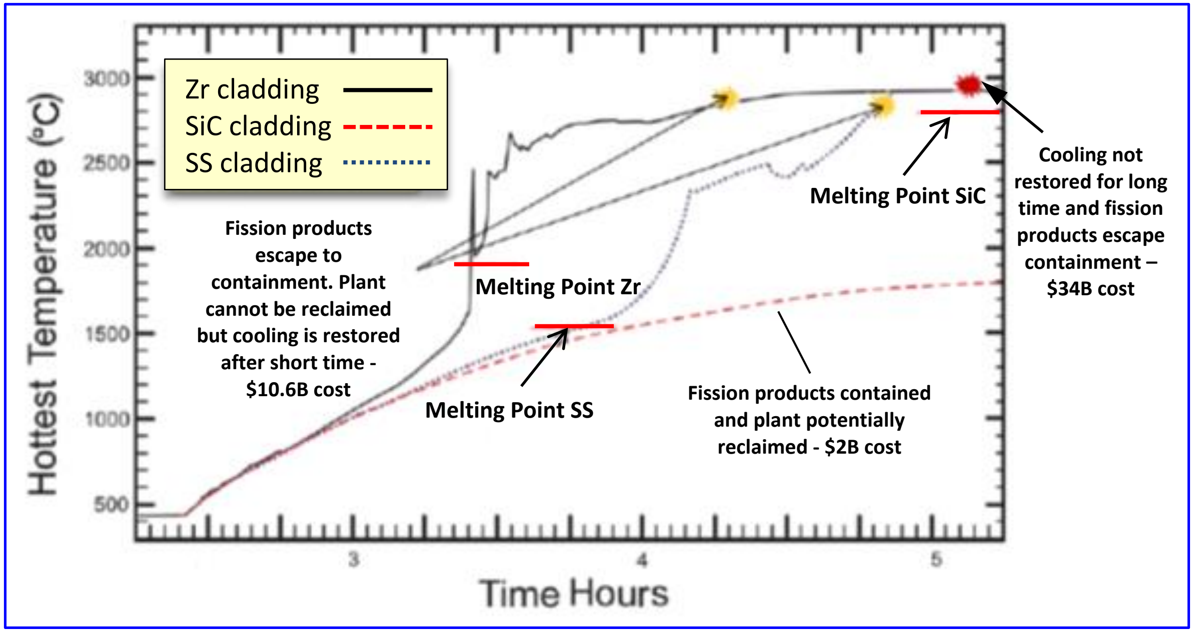
Outline

- General Introduction
  - Why MAX Phases?
  - MAX Phases for Advanced Nuclear Systems
- MAX Phases for Gen-IV LFRs: MYRRHA Pump Impeller
  - Nb-Al-C System: Nb_4AlC_3
  - Nb-Zr-Al-C System: $(Nb,Zr)_4AlC_3$
  - Processing towards Mechanical Property Optimization
  - Resistance to Dissolution Corrosion in LBE
  - Resistance to Flow-Assisted Corrosion in LBE
- MAX Phases for Gen-III+ LWRs: Accident-Tolerant Fuels (ATFs)
  - Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC
- Conclusions

MAX Phases for Gen-III+ LWRs: Accident-Tolerant Fuels (ATFs)

KU LEUVEN
Université de Poitiers
SCK•CEN STUDIECENTRUM VOOR KERNENERGIE CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE
LINKÖPINGS UNIVERSITET
Drexel UNIVERSITY

MAX Phases for ATF Cladding Materials



Problem Setting:

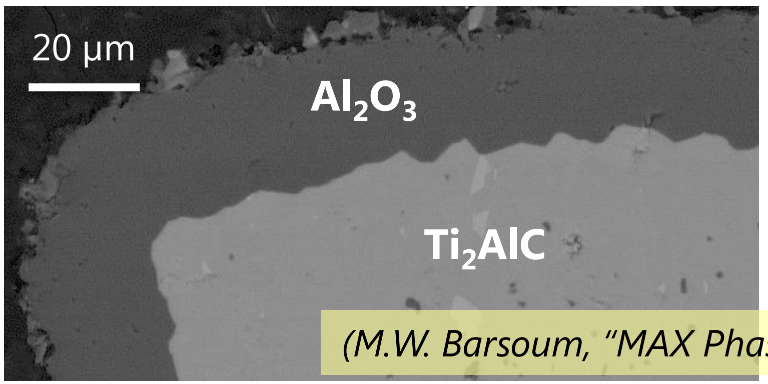
- Loss of coolant & runaway exothermic zircalloy clad/water reactions → cladding failure
- Release of fission products to containement & plant loss
- Release of hydrogen & possible hydrogen explosion
- Escape of radioactive fission products beyond site boundary
- Plant loss & high remediation cost of surrounding area

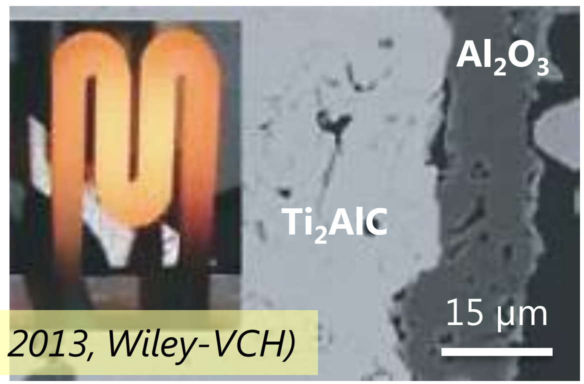
(E. Lahoda et al., Ref #: RT-TR-14-6, Paper nr 10231, 2014, Westinghouse Electric Company LLC)

- Use MAX phases coatings on commercial cladding materials to:
  - Achieve step enhancement in performance of current cladding materials during nominal operation conditions & short-lived design-basis transients (<1200°C)
  - Maintain hermeticity for prolonged periods (hours to days) under beyond-design-basis accidents (1200-1700°C) conditions – very challenging

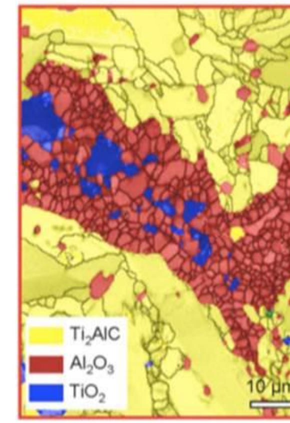
Potential of MAX Phases for ATF Clads

- Certain MAX phases (e.g. Ti_2AlC, Cr_2AlC) form a protective oxide scale (Al_2O_3) that does not spall off during thermal cycling (e.g. Ti_2AlC, 8000 cycles to 1350°C in air)
- MAX phases show self-healing of cracks in oxidizing environments
- Self-healing potential for radiation-induced defects!

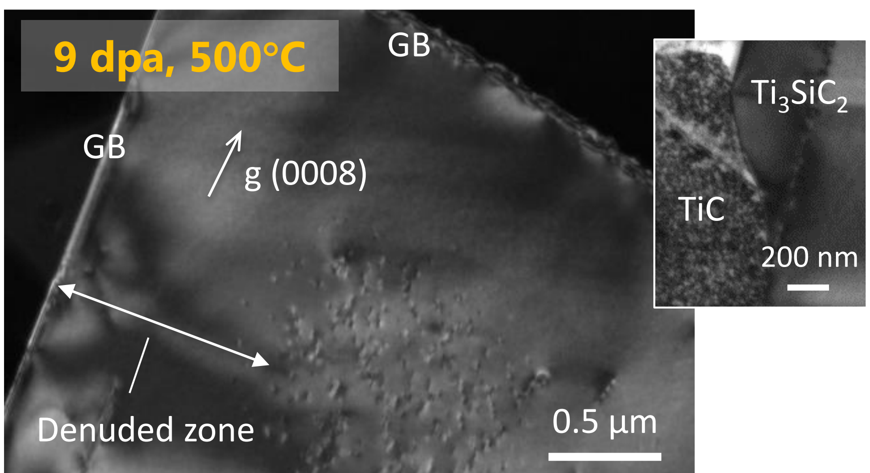


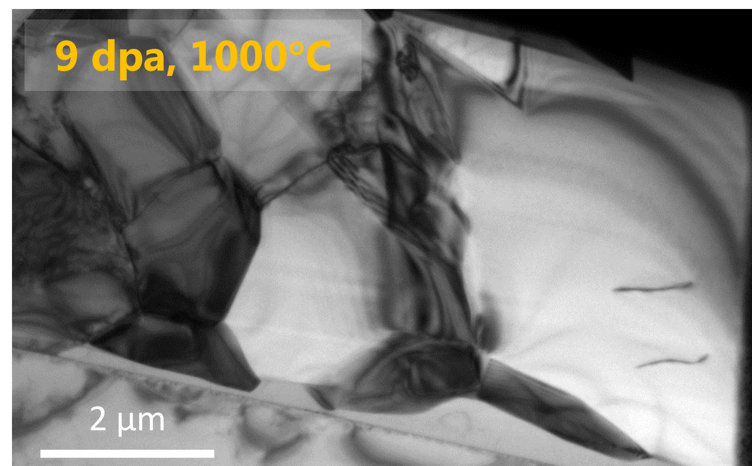


(M.W. Barsoum, "MAX Phases", 2013, Wiley-VCH)



Ti_3SiC_2



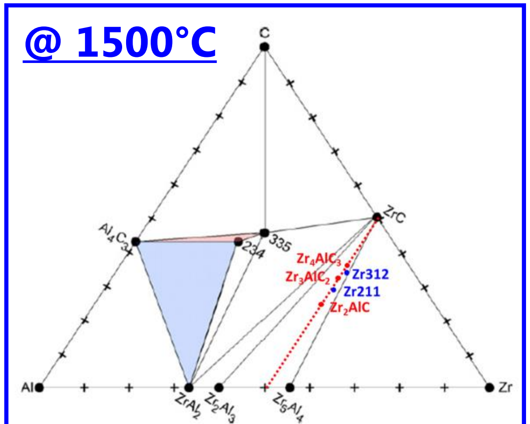


(Courtesy: D.J. Tallman, M.W. Barsoum)

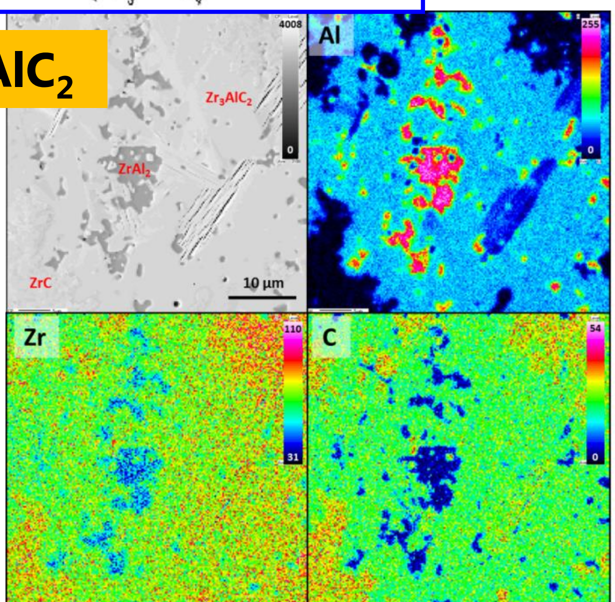
KU LEUVEN

Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC

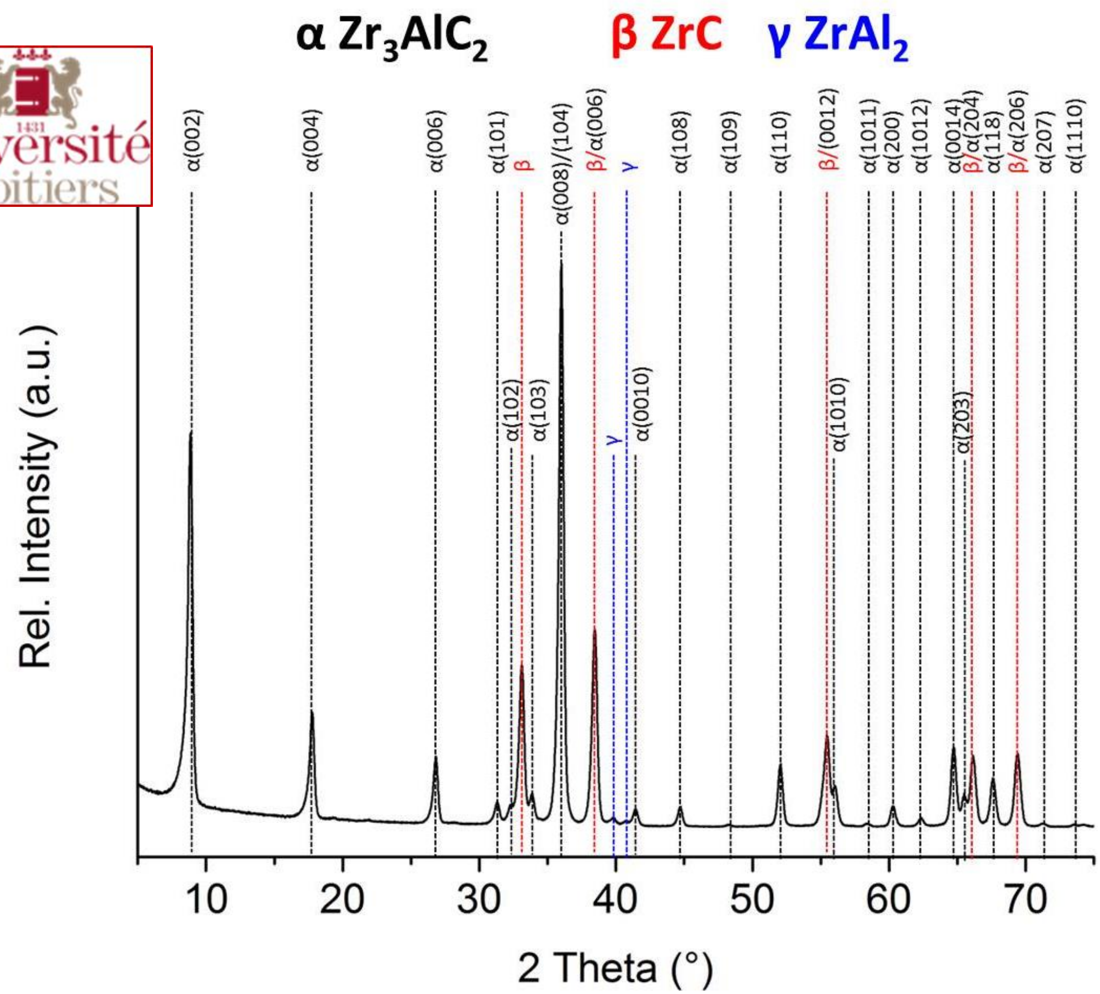
- No MAX phases were synthesized before in the Zr-Al-C system!



Zr_3AlC_2



Université de Poitiers



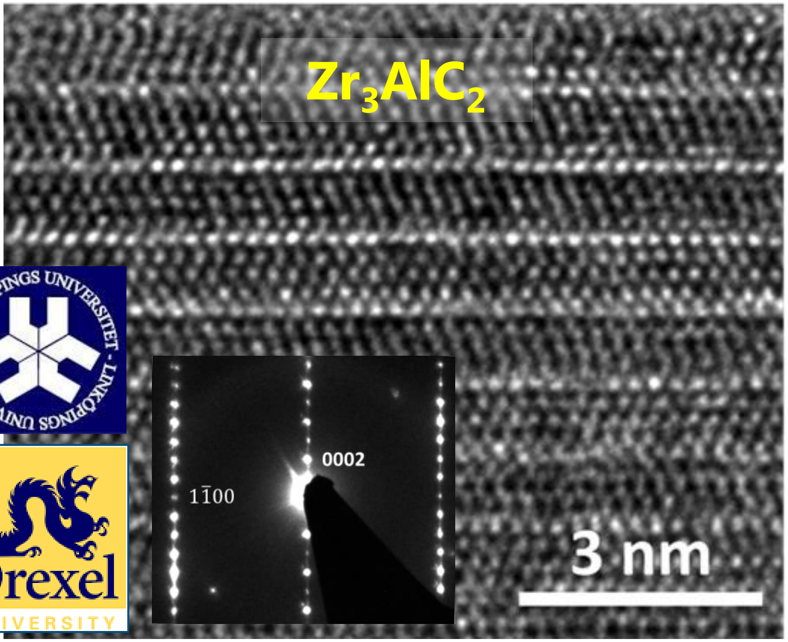
(*Courtesy:* *T. Cabioc'h*)

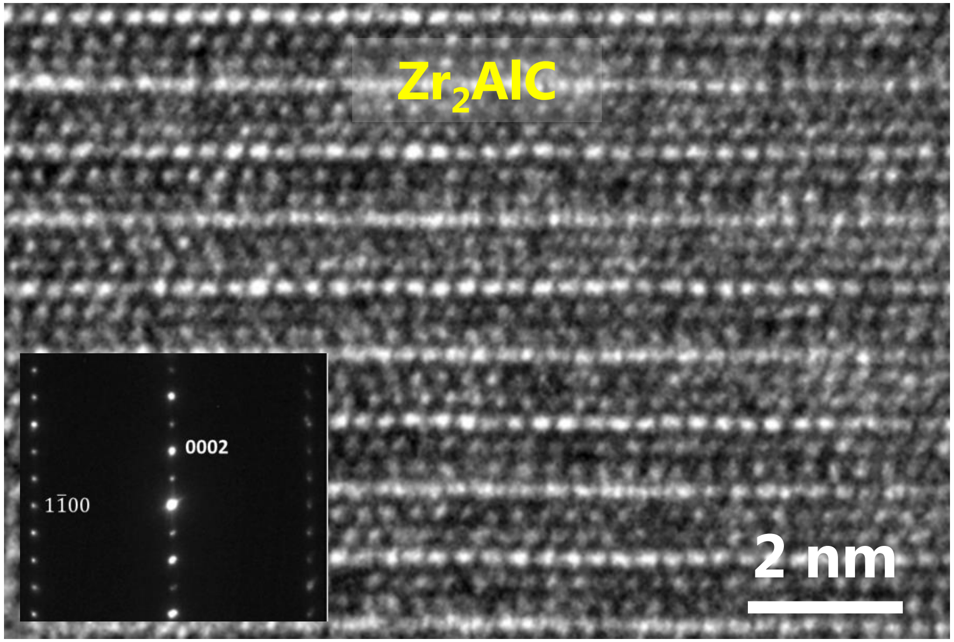
Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC

➢ Lattice parameters determined by XRD and confirmed by HRTEM

Zr_3AlC_2	
Space group	$P6_3/mmc$ (194)
Lattice	Hexagonal
a (Å)	3.33308(6)
c (Å)	19.9507(3)

Zr_2AlC	
Space group	$P6_3/mmc$ (194)
Lattice	Hexagonal
a (Å)	3.3237(2)
c (Å)	14.5705(4)





(*Courtesy:* *J. Lu, L. Hultman, J. Halim, M.W. Barsoum*)

Outline

- General Introduction
  - Why MAX Phases?
  - MAX Phases for Advanced Nuclear Systems
- MAX Phases for Gen-IV LFRs: MYRRHA Pump Impeller
  - Nb-Al-C System: Nb_4AlC_3
  - Nb-Zr-Al-C System: $(Nb,Zr)_4AlC_3$
  - Processing towards Mechanical Property Optimization
  - Resistance to Dissolution Corrosion in LBE
  - Resistance to Flow-Assisted Corrosion in LBE
- MAX Phases for Gen-III+ LWRs: Accident-Tolerant Fuels (ATFs)
  - Zr-Al-C System: Zr_3AlC_2 & Zr_2AlC
- Conclusions

Conclusions

- Exploring the potential of MAX phases as *candidate materials for specific applications in advanced nuclear systems* entails the following challenges:

  i. Control of material processing to produce stable phase mixtures that meet the targeted material property requirements (strength, fracture toughness, fatigue resistance) of the end application (e.g. MYRRHA pump impeller)

  ii. Mechanical testing on the produced materials both in inert/air and heavy liquid metal (Pb/LBE) environments to detect possible environment-assisted material degradation effects (e.g. liquid metal embrittlement)

  iii. LMC/erosion testing on the produced materials at various test conditions (T, [O], time, flow velocity) so as to understand their behavior

  iv. Cladding/coolant interaction tests in various coolant states (water, steam) to assess their behavior in service (e.g. ATF cladding materials)

  v. Screening neutron irradiation campaigns must be designed and performed so as to assess the neutron irradiation tolerance of the produced materials (the criticality of this study depends on the envisaged component, e.g. pump impeller vs. cladding material)


Thank you for your attention!
Questions?

SCK•CEN
Studiecentrum voor Kernenergie
Centre d'Etude de l'Energie Nucléaire
Belgian Nuclear Research Centre

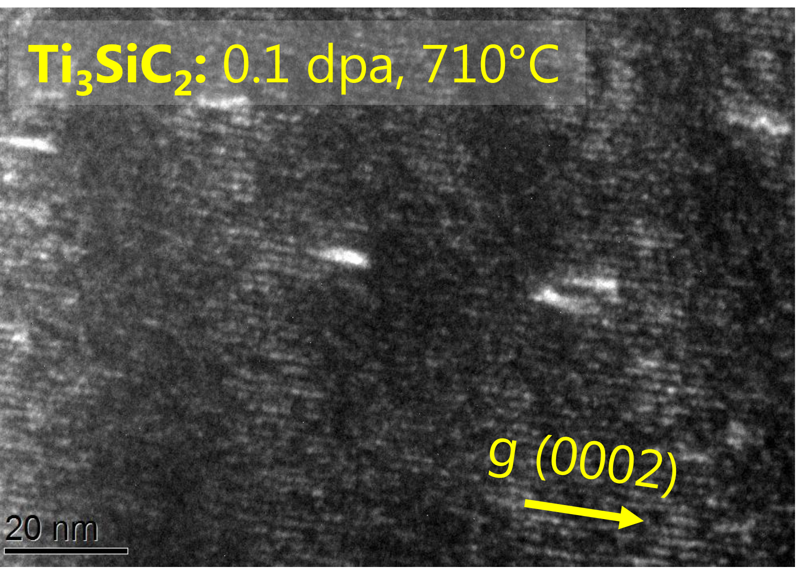
Stichting van Openbaar Nut
Fondation d'Utilité Publique
Foundation of Public Utility

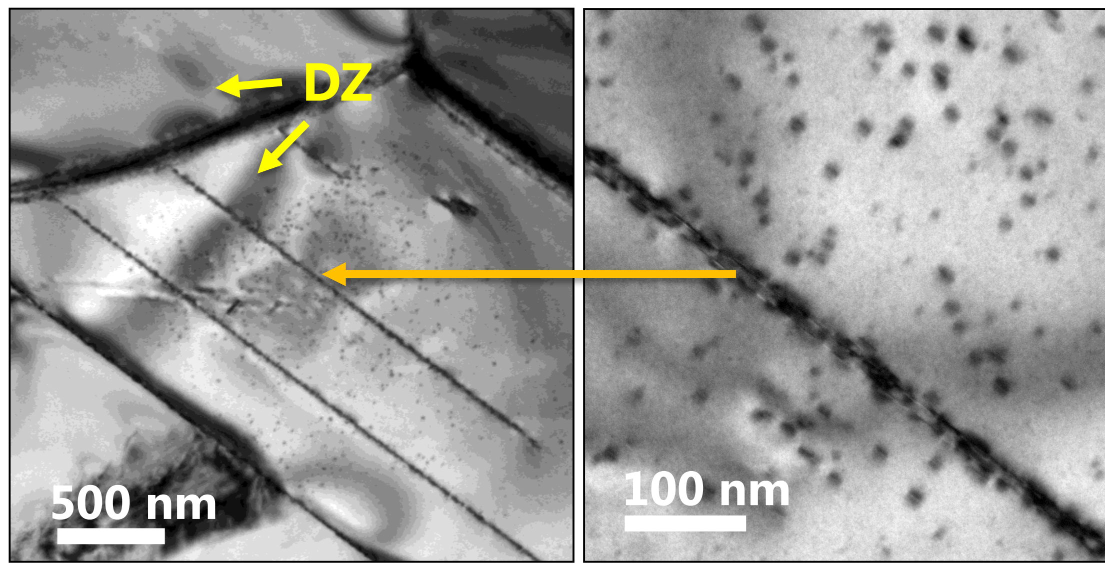
Registered Office: Avenue Herrmann-Debrouxlaan 40 – BE-1160 BRUSSELS
Operational Office: Boeretang 200 – BE-2400 MOL

SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Neutron Irradiation of MAX Phases

- Investigation of the effect of neutron irradiation on MAX phases:
  - Formation of dislocations loops: $\mathbf{b} = \frac{1}{2}[0001]$ in the basal plane
  - **Denuded zones (DZ)**: nearly defect-free regions close to grain boundaries
  - Defect clusters are found near stacking faults





(*Courtesy:* *D.J. Tallman, M.W. Barsoum*)

Processing of MAX Phases

- Mixing of Al and C can result in formation of Al_4C_3

  $$Al_4C_3 + 12\ H_2O_{hum} \rightarrow 3\ CH_4 + 4\ Al(OH)_3$$

- Need for fine Nb powder

  At 700°C: $$3\ Al(l) + Nb(s) \rightarrow NbAl_3(s)$$

- Break-up of commercial, coarse Nb (~300 µm)
  - Ball-milling: resulted in Nb flakes
  - Hydrogenating + Ball Milling

    At 800°C: $$Nb(s) + H_2(g) \rightarrow NbH_{0.89}(s)$$