MAX Phases for Gen-IV Lead Fast Reactors (LFRs)

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The 5th Huddersfield Annual Accelerator Symposium:

Announcing the **UK National Ion Beam Centre**

Buckley Lecture Theatre, U Huddersfield, 21/04/2017

Outline

- Introduction
  - Starting R&D Point: MYRRHA
  - Envisaged Applications for MYRRHA & Gen-IV LFRs
  - Why MAX Phases for MYRRHA & Gen-IV LFRs?
- MAX Phase Synthesis: Application-Driven
  - Phase Purity: Zr-Al-C System vs. (Zr,Nb)-(Al,Sn)-C System
  - Oxidation Resistance: (Zr,Ti)-Al-C System
  - Mechanical Properties: (Nb,Zr)-Al-C System
- MAX Phase Compatibility with Liquid LBE
  - Compatibility with Static LBE
  - Compatibility with Fast-Flowing LBE
- Mechanical Properties of MAX Phases
- Exploratory Ion Irradiation of $(Nb_{0.85},Zr_{0.15})_4AlC_3$
- Conclusions

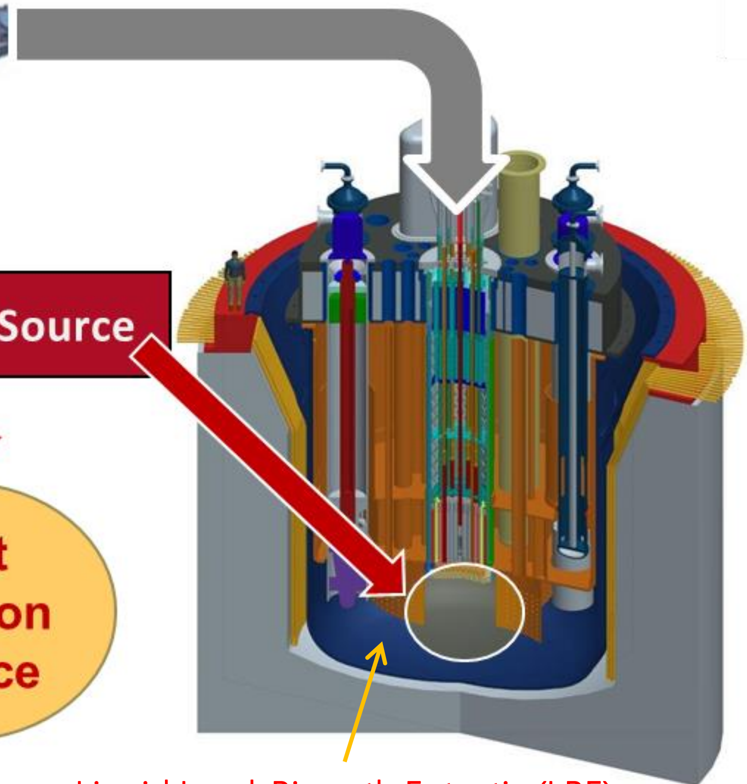
MAX Phase R&D Starting Point: MYRRHA

Accelerator

(600 MeV - 4 mA proton)

Reactor

- Subcritical or Critical modes
- 65 to 100 MWth



MYRRHA Stainless Steels

- 316L: structural steel
- DIN 1.4970: fuel cladding steel

Spallation Source

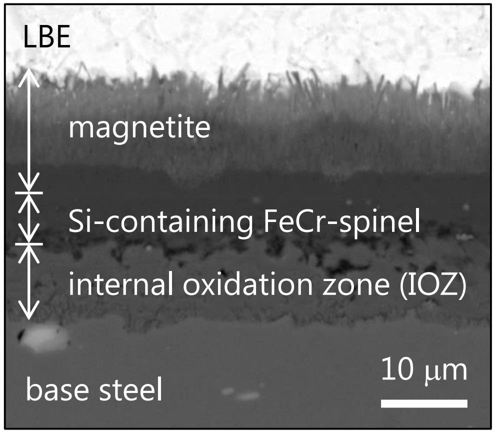
Fast Neutron Source

Multipurpose Flexible Irradiation Facility

Liquid Lead-Bismuth Eutectic (LBE) Primary Coolant

Basic Liquid Metal Corrosion (LMC) Mechanisms

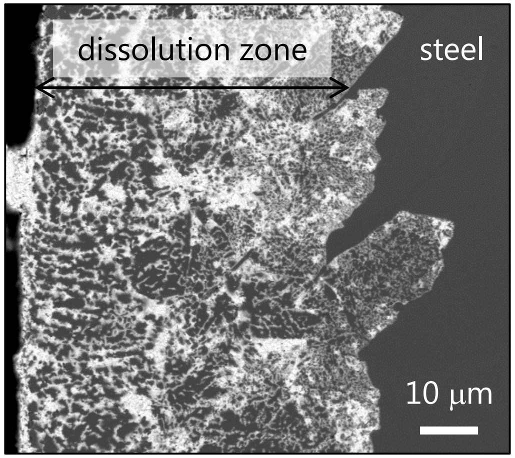
1. Oxidation



- Multi-layered oxide scales form in contact with O-containing LBE on steel surface
- If protective at service conditions, oxide scales minimize further attack of steel by LBE

EP-823: 490°C, 5016 h, oxygen saturation, static LBE
(K. Lambrinou, SCK•CEN)

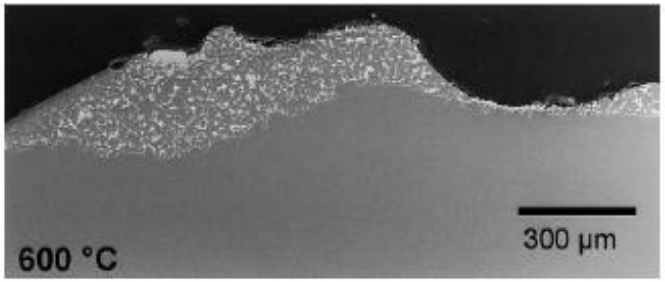
2. Dissolution



- Loss of steel alloying elements (Ni, Mn, Cr)
- LBE penetration
- Ferritization of dissolution zone due to loss of austenite stabilizers (Ni, Mn)

316L: 500°C, 3282 h, 7.5×10^{-13} < [O] (mass%) < 2.8×10^{-8}, static LBE *(K. Lambrinou, SCK•CEN)*

3. Erosion

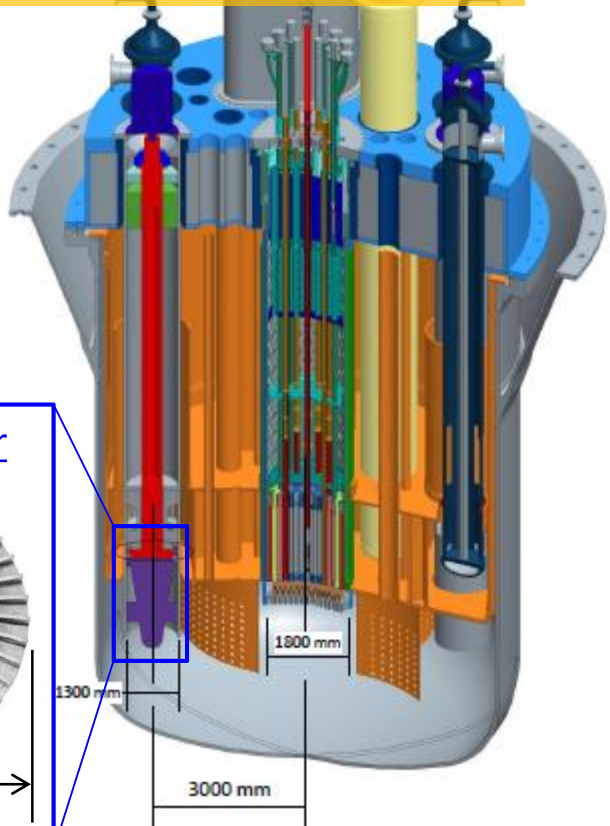


- Severe material loss & compromise of structural integrity
- Observed at high LBE flow velocities, two-phase flow, and sites of flow diversion

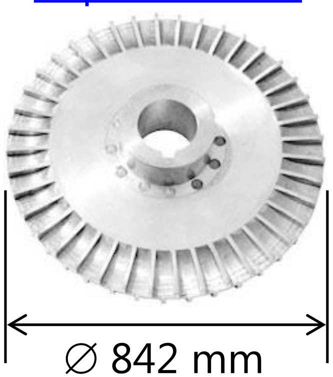
316L: 600°C, 2000 h, [O] ≈ 10^{-6} mass%, flowing LBE (v ≈ 2 m/s)
*(Müller et al., Journal Nuclear Materials **301** (2002) 40-46)*

Envisaged Applications for MYRRHA & Gen-IV LFRs

- **MYRRHA Pump Impeller Service Conditions:**
  - T ≈ 270°C (T ≈ 480°C in Gen-IV LFRs)
  - High LBE flow velocity (v ≈ 10-20 m/s)
  - LBE [O] ≈ 10^{-6} mass%
  - Low fast neutron dose (< 1 dpa)

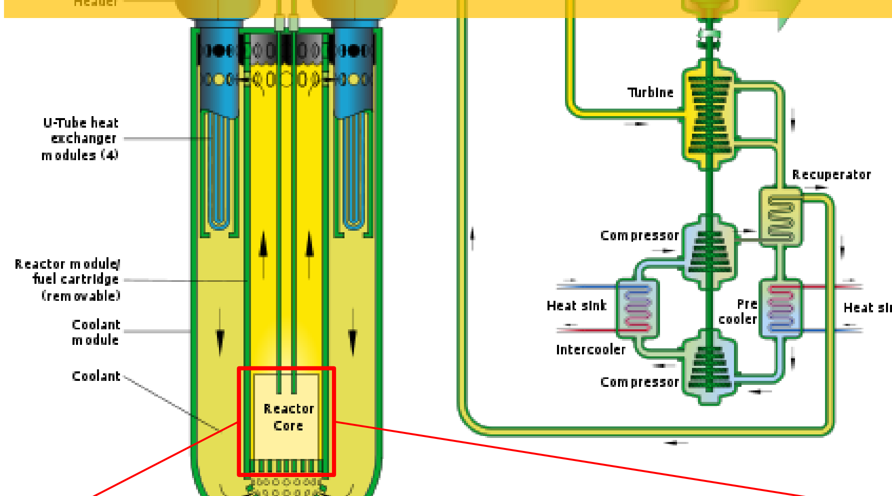


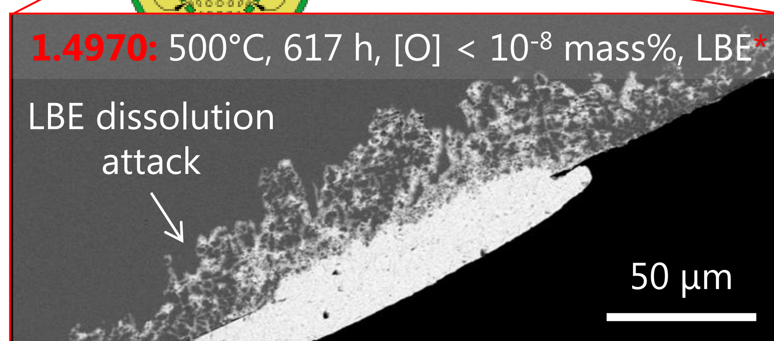
Impeller Rotor



Gen-IV LFR Fuel Cladding Materials

- **Gen-IV LFR Fuel Clad Requirements:**
  - Liquid metal corrosion resistance at T > 450°C
  - Neutron radiation tolerance ($dose_{EOL}$ > 35 dpa)
  - Controlled oxidation for effective heat removal

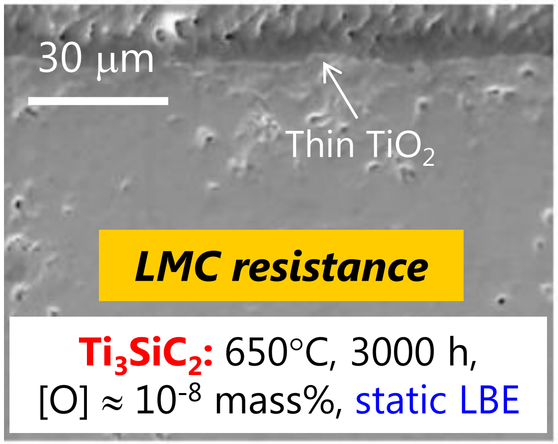




❖ Not actual MYRRHA pump impeller design!

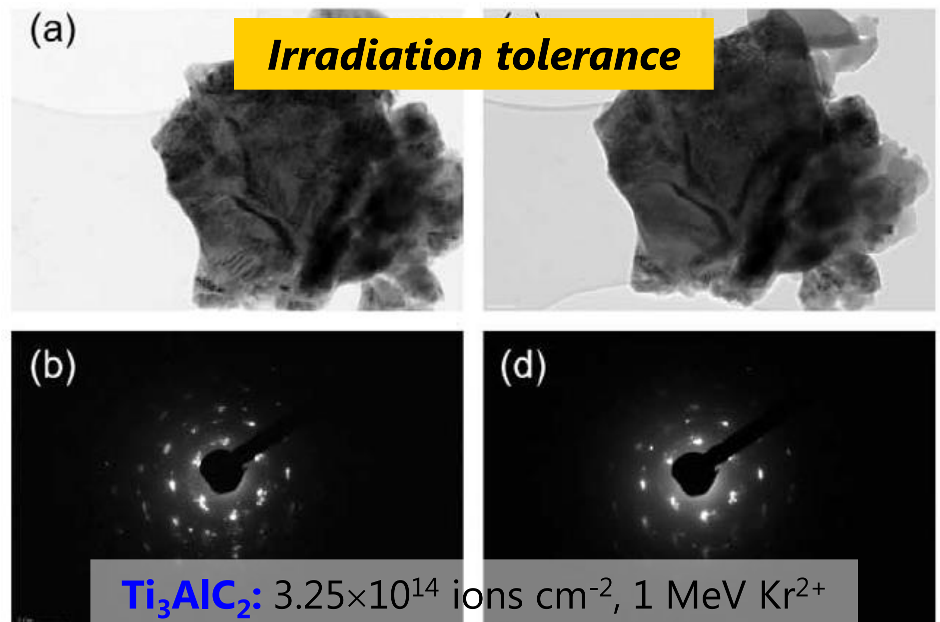
Why MAX Phases for MYRRHA & Gen-IV LFRs?

- MAX Phases: unique combination of physical, chemical, mechanical properties, e.g., LMC resistance, machinability, damage tolerance, irradiation tolerance, …



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

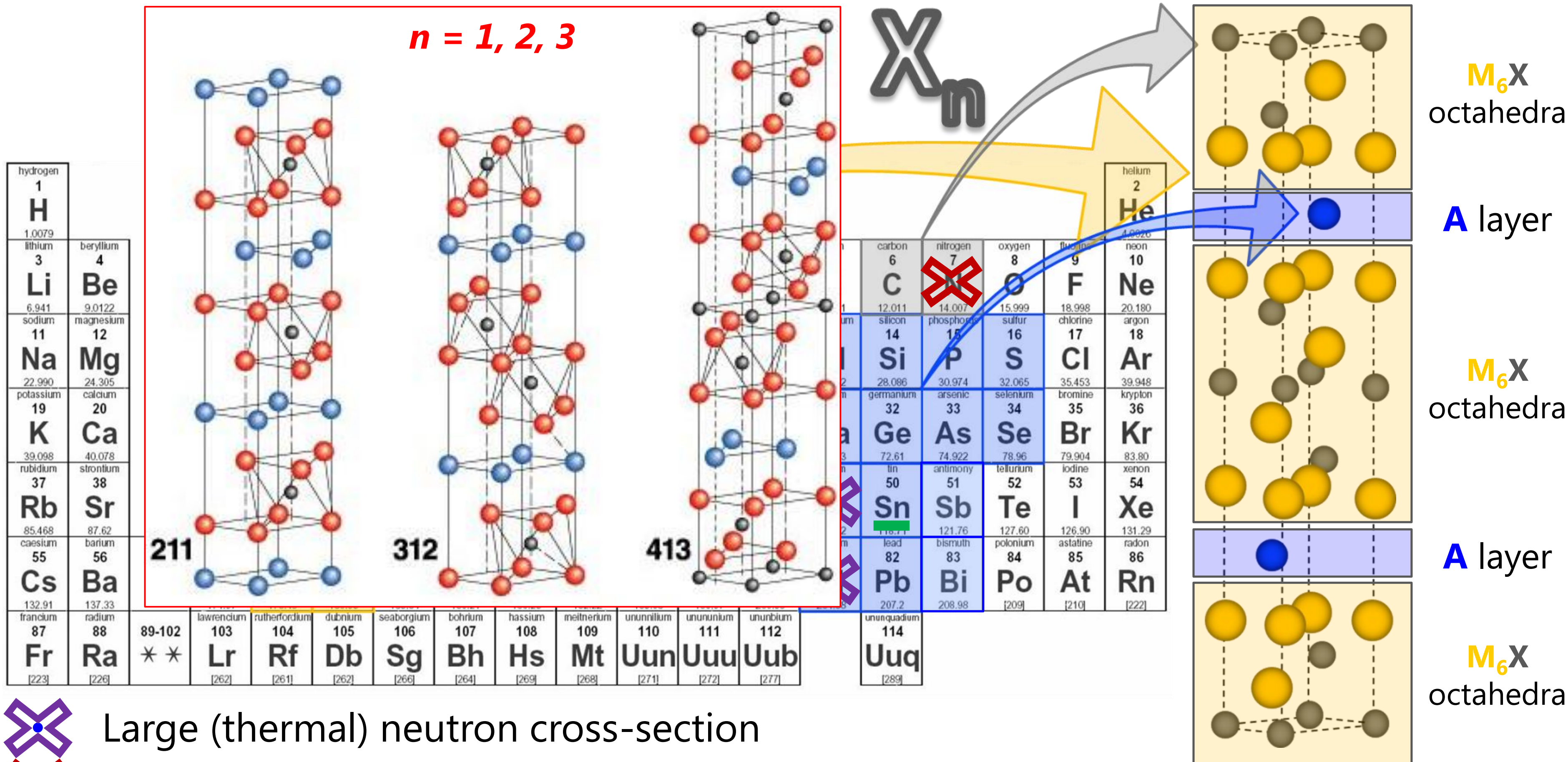
*(M.W. Barsoum & M. Radovic, Annu. Rev. Mater. Res. **41** (2011) 195-227)*



*(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 ($M_{n+1}AX_n$) Phases: Elemental Preselection

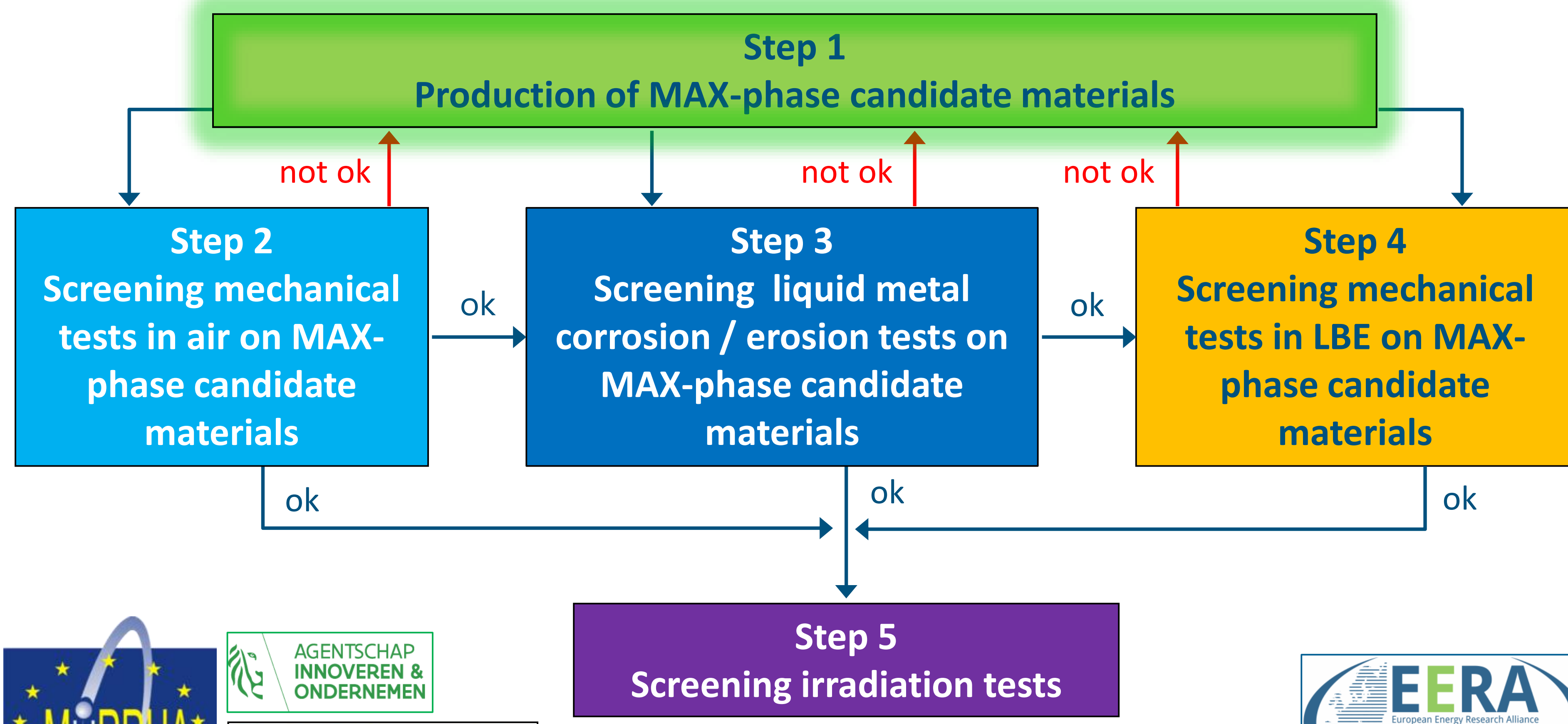


Laminated crystal structure

- Large (thermal) neutron cross-section
- Long-lived isotope [14]C
- Alloying elements in commercial clads (zircaloys/15-15Ti stainless steels)

➢ System of interest: **Zr-Al-C** and **solid solutions thereof (+Nb, Ti, Cr, Sn, …)**

MAX Phase R&D: Approach, Challenges, Achievements



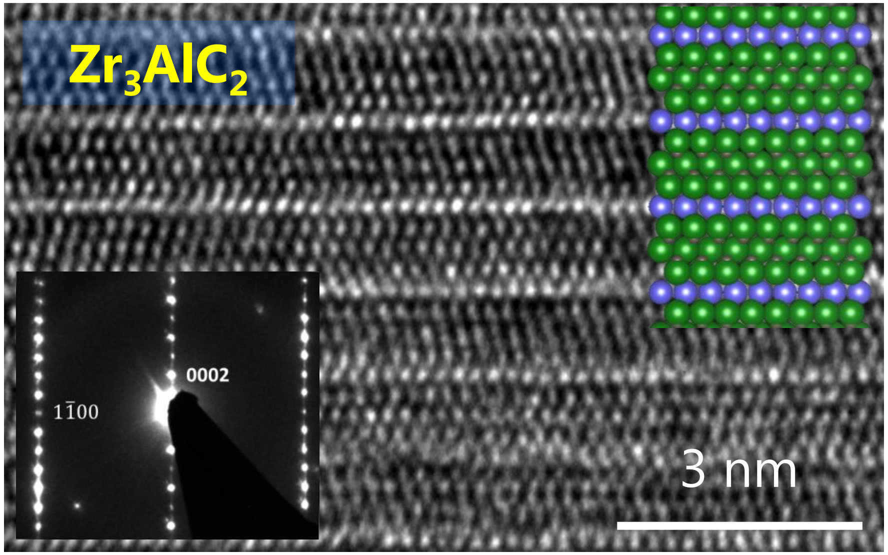
STEP 1

Synthesis: Zr-Al-C System

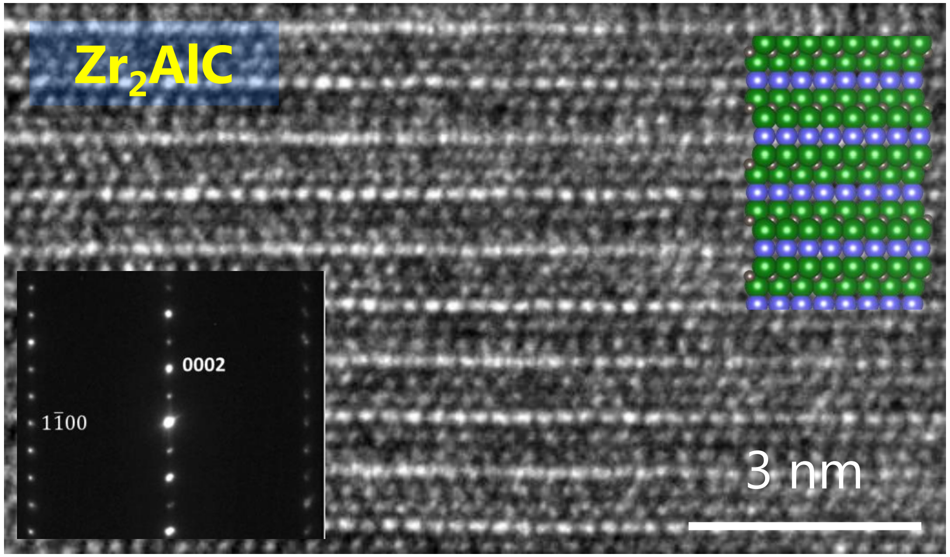
- Discovery (synthesis) of MAX phases in the Zr-Al-C system!
- Synthesis facilitated by the use of finer starting powders (ZrH_2, Al & C)
- Production of phase-pure Zr-based MAX phases proved challenging

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

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



(T. Lapauw et al., J. Eur. Ceram. Soc. **36** (2016) 943–947)



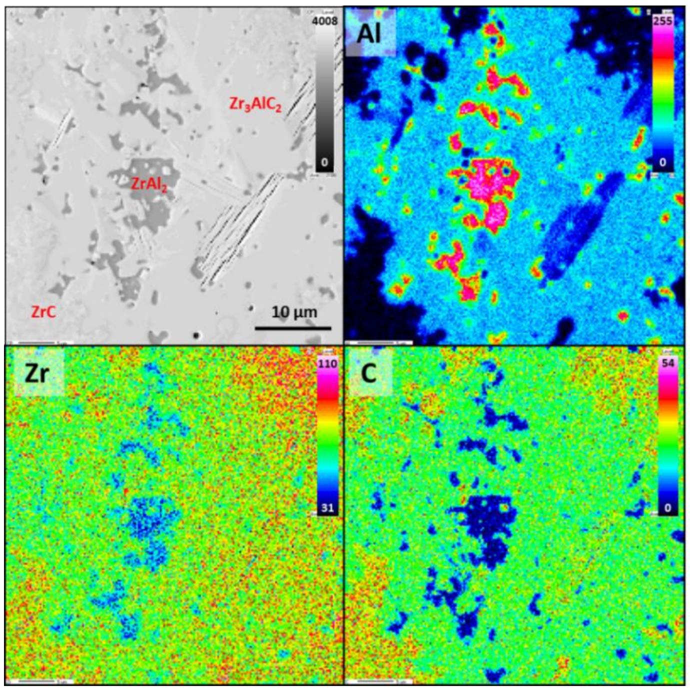
(T. Lapauw et al., J. Eur. Ceram. Soc. **36** (2016) 1847–1853)

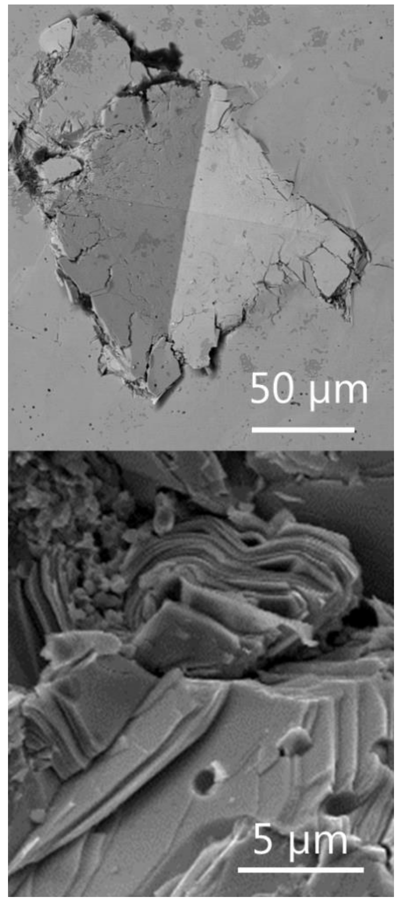
STEP 1

Zr-Al-C System Challenge: Phase Purity

Starting ratio: Zr:Al:C = 51.0 : 15.9 : 33.1

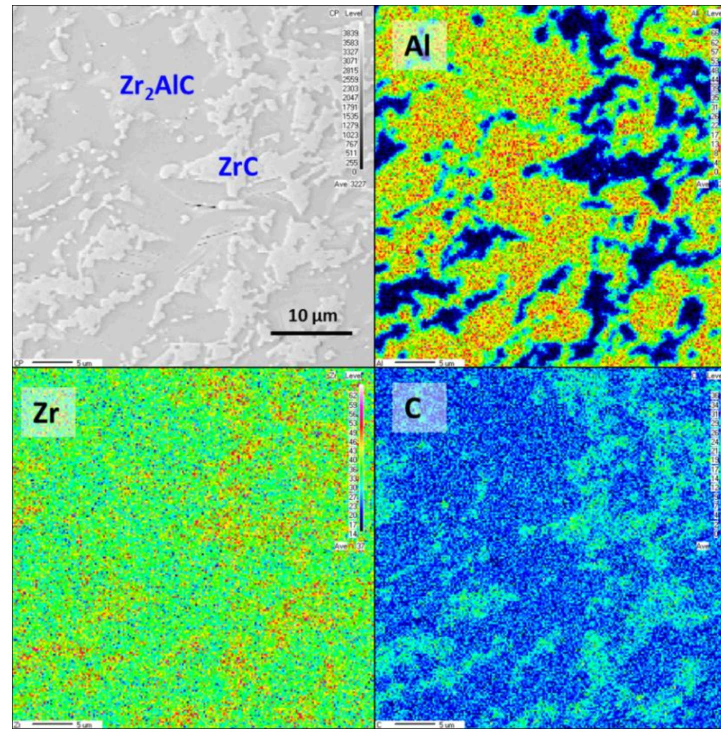
Phase	Weight%
Zr_3AlC_2	59(1)
ZrC	35(1)
$ZrAl_2$	6(1)





Zr:Al:C = 50 : 20 : 30

Phase	Weight%
Zr_2AlC	67(1)
ZrC	33(1)



- Phase purity: minimises differences in swelling, corrosion behaviour, etc.
- Synthesis of $(M,M')_{n+1}(A,A')X_n$ solid solutions to increase phase purity!

STEP 1

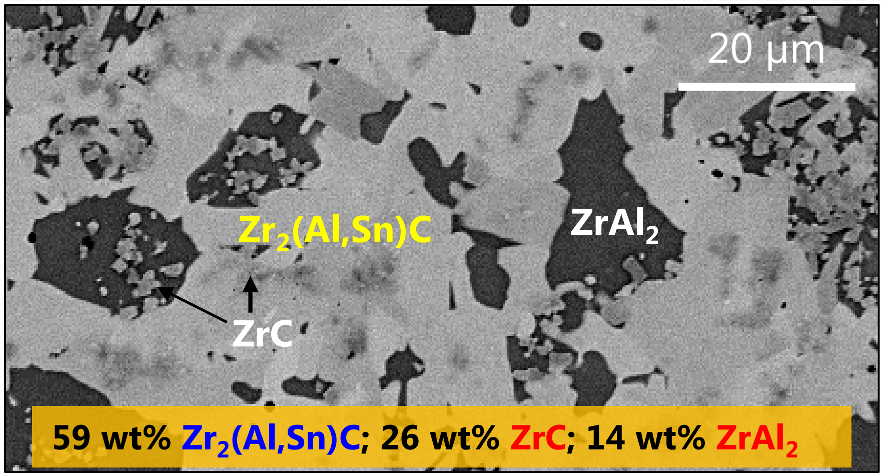
High Phase Purity: (Zr,Nb)-(Al,Sn)-C SS

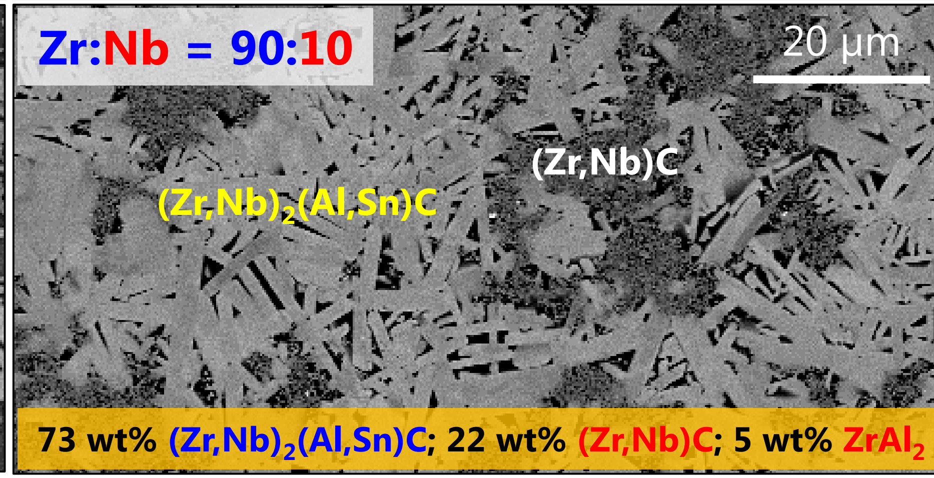
- Best Zr_2AlC-based material contained 67 wt% Zr_2AlC & 33 wt% ZrC

Sn was selected as most promising alloying A-element in $Zr_2(Al_{1-x},A_x)C$

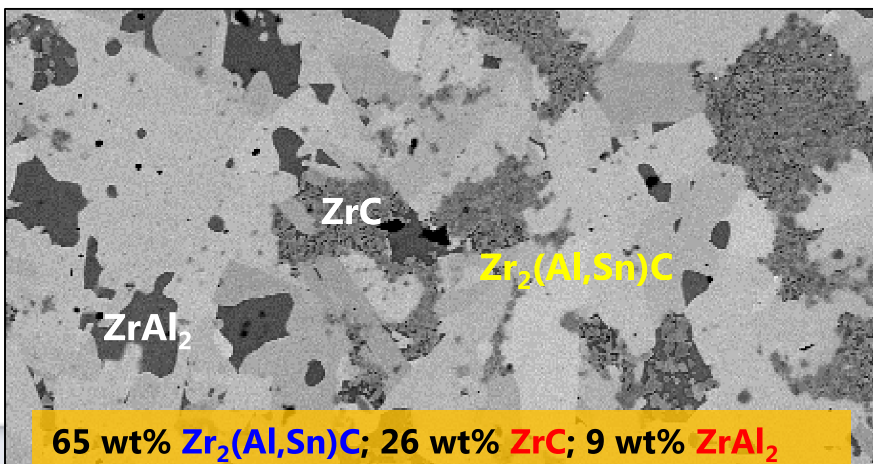
Solid solution on both M and A sites: $(Zr_{1-x},Nb_x)_2(Al_{1-x},Sn_x)C$

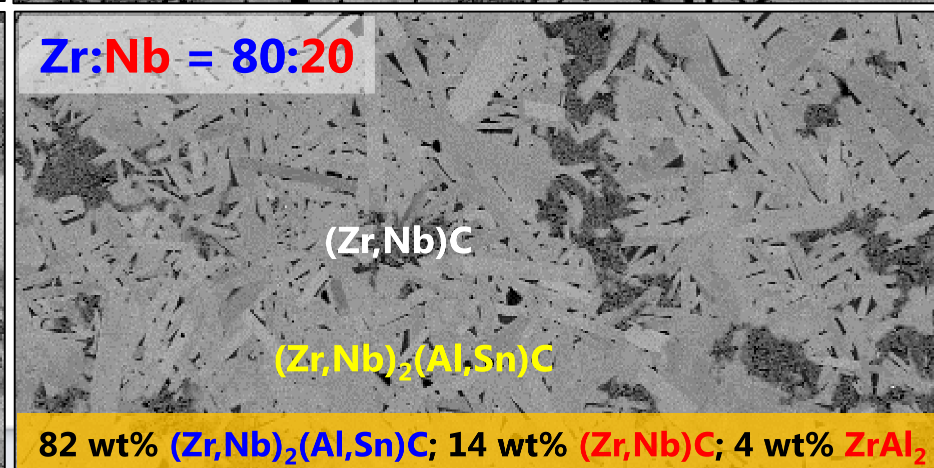
Al:Sn = 85:15





Al:Sn = 75:25

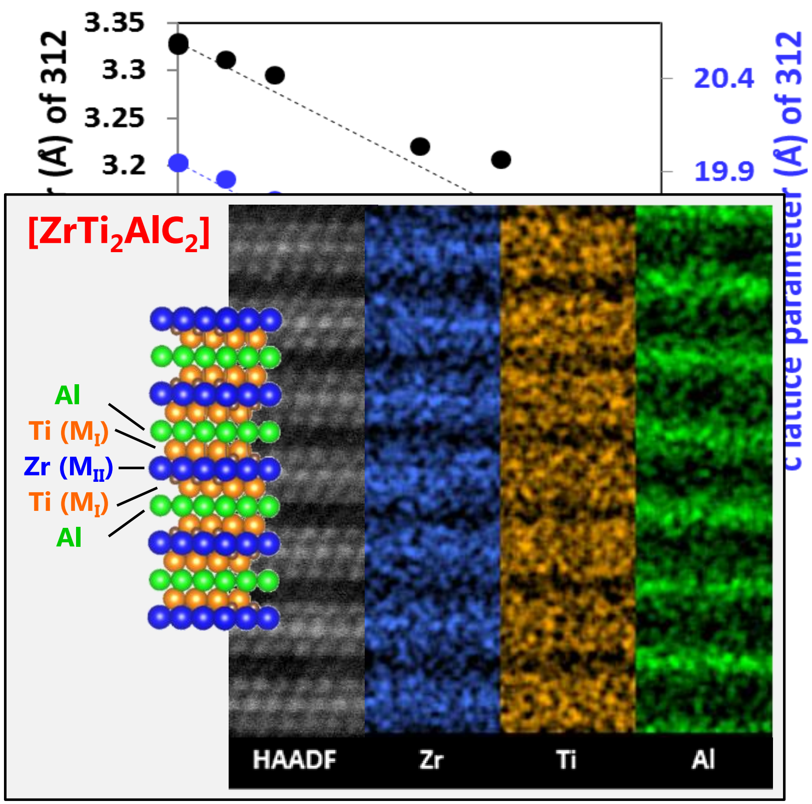


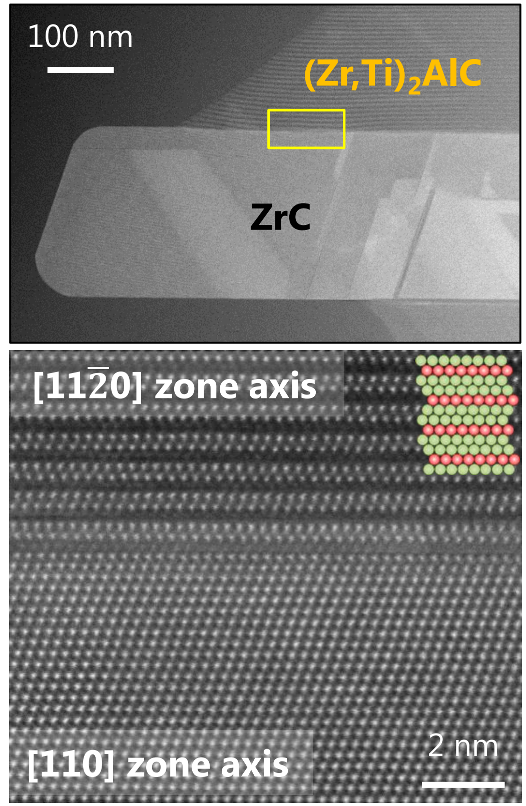


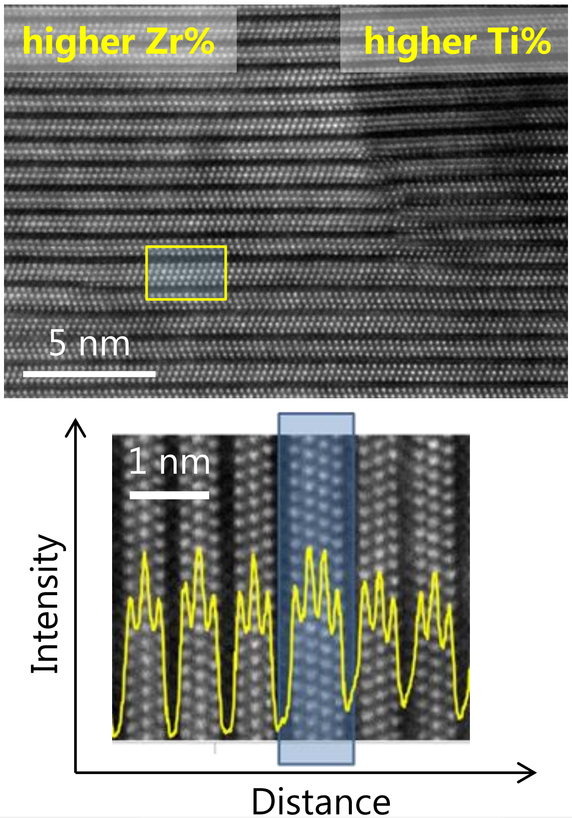
STEP 1

Oxidation Resistance: (Zr,Ti)-Al-C SS

- Investigation of **Ti** solubility in $Zr_{n+1}AlC_n$ by *reactive hot pressing*
  - Solid solubility over the entire compositional range for both 211 & 312
  - Atomic ordering in both 312 & 413 stackings: Ti on M_I site & Zr on M_{II} site
  - Non phase-pure MAX phase ceramics (Zr_2Al_3, $ZrAl_3$, (Zr,Ti)C)



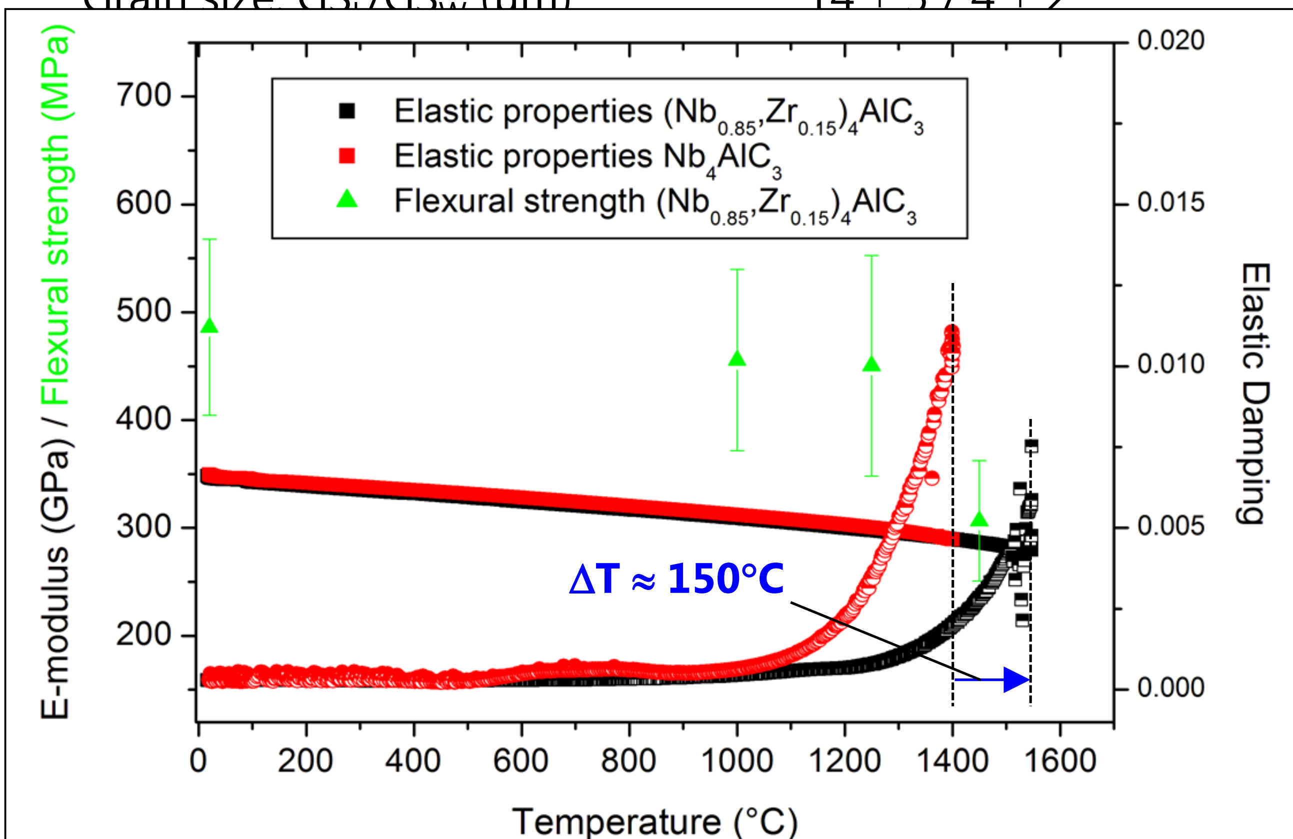




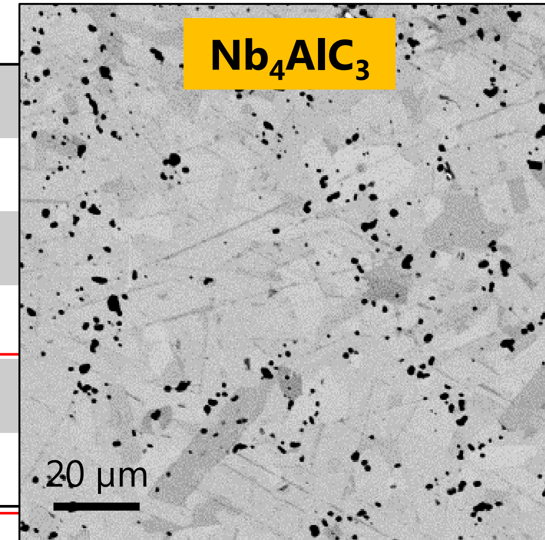
STEP 1

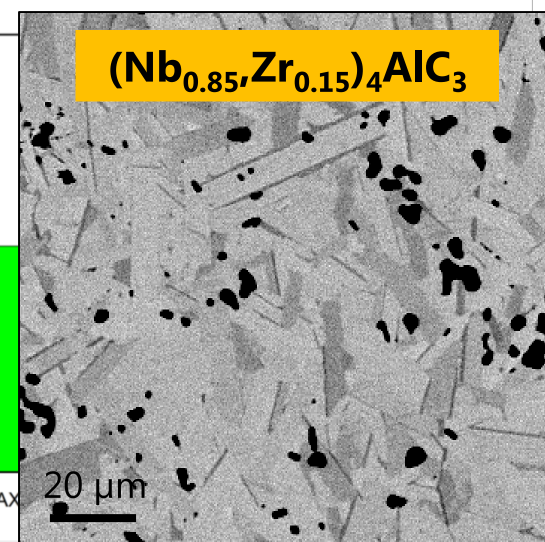
Mechanical Properties: (Nb,Zr)-Al-C SS

Property	Nb_4AlC_3
ρ (g/cm^3)	6.89 ± 0.06 (98% ρ_{th})
Grain size: GS_L/GS_W (μm)	14 ± 5 / 4 ± 2

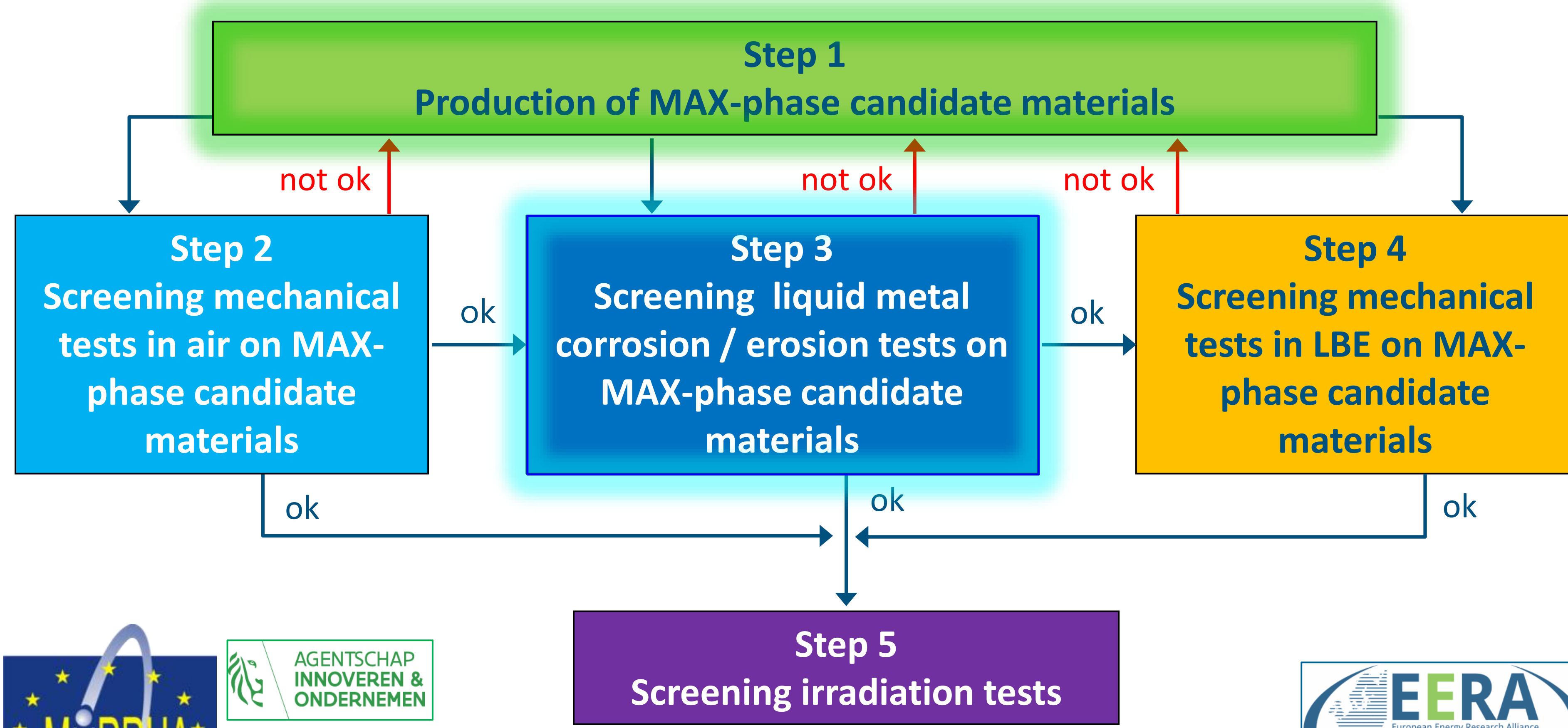


MAXTHAL 312® MAXTHAL 211® Nb_4AlC_3 $(Nb_{0.85},Zr_{0.15})_4AlC_3$ MAXTHAL 312® MAX





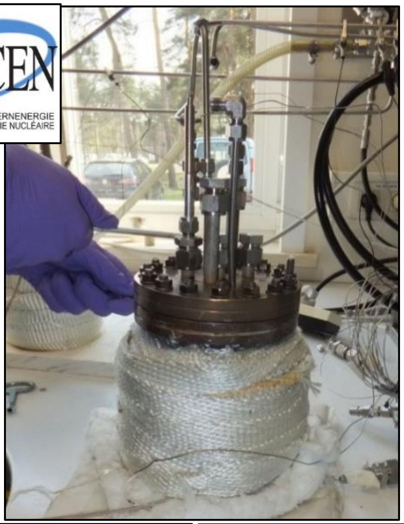
MAX Phase R&D: Approach, Challenges, Achievements

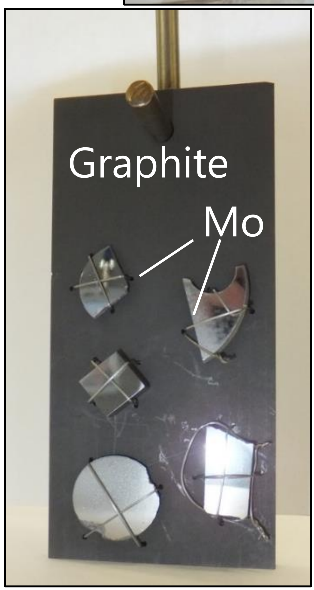


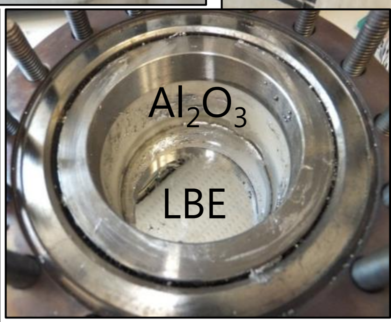
STEP 3

LMC/Erosion: Test Setups

LMC Setup

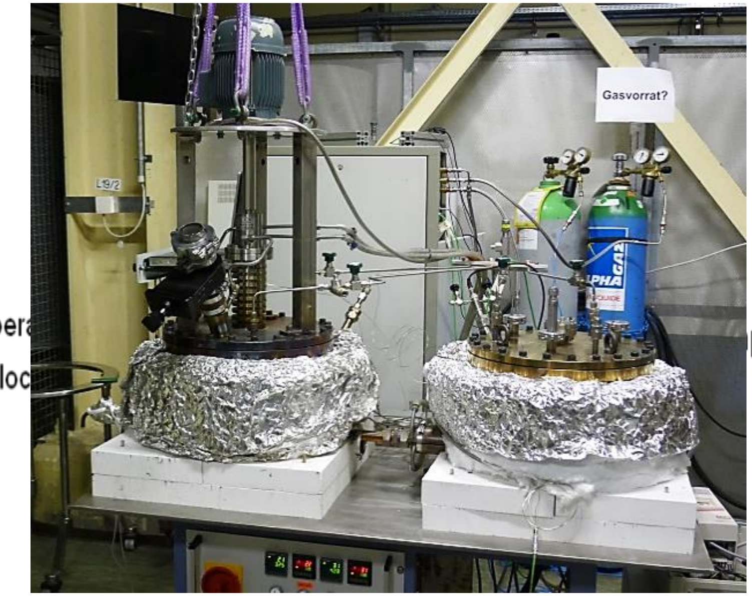






- **Tests:** MAX phases vs. 316L; test conditions promoting dissolution attack (500°C, [O] < 10^{-9} mass%, 1000-3500 h, static LBE)

- **Erosion Setup – CORELLA facility:**
  - Fast-flowing Pb/LBE (v > 10 m/s)
  - T & [O] (SCK•CEN oxygen sensor)
  - Control [O] by using conditioning gases
- Tests: MAX phases & 316L stainless steel (ref); relevant for MYRRHA (300°C) & Gen-IV LFR (500°C) impellers (v > 8 m/s)

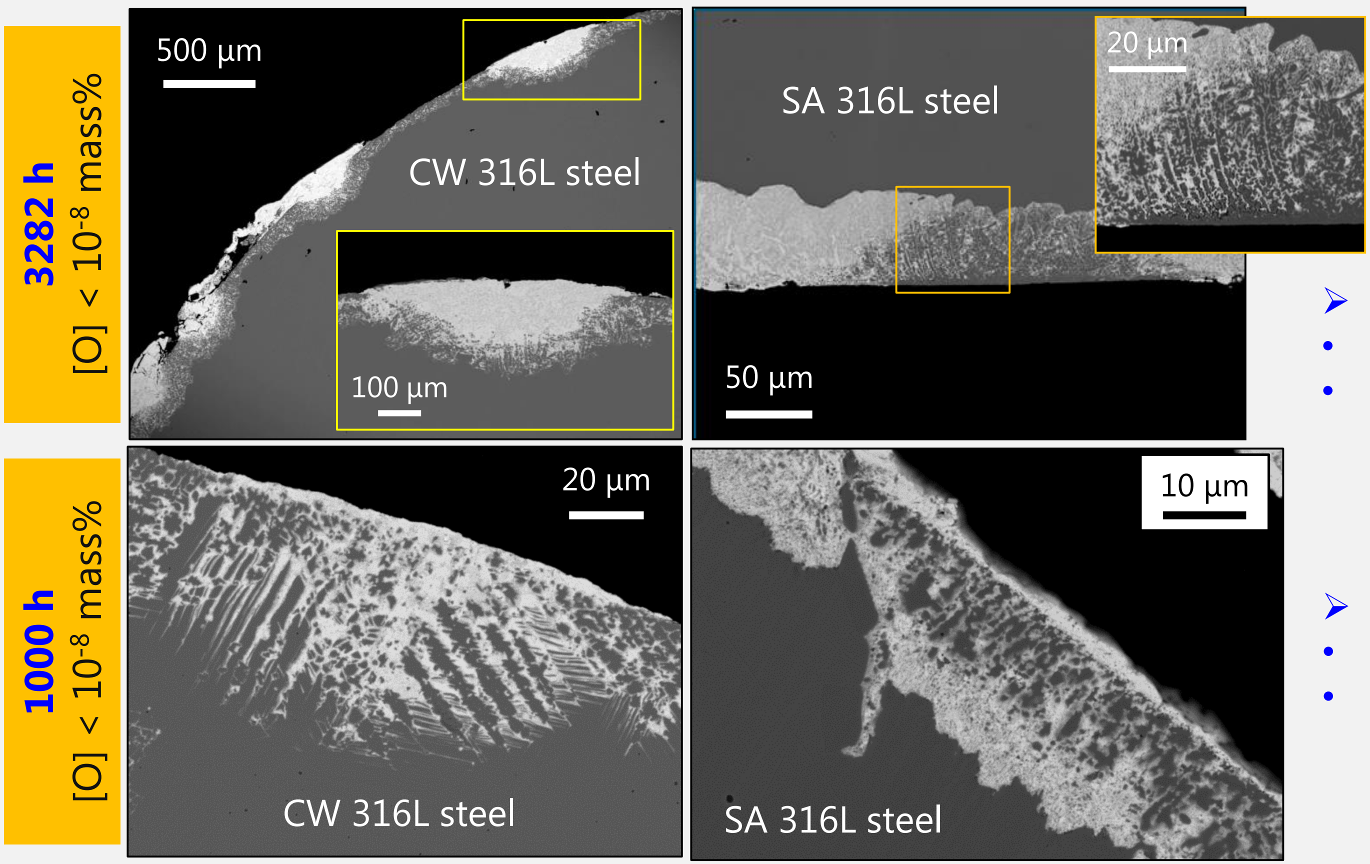


TCh: test chamber; CCh: conditioning chamber

* **CORELLA:** Corrosion Erosion Facility for Liquid Lead Alloy

STEP 3 Compatibility with Static LBE (LMC)

- Aim: to assess MAX phase compatibility with static, oxygen-poor LBE:
  - 500°C, 3500 h, [O] < 10^{-9} mass%; Maxthal 211® & 312®, Nb_2AlC, Nb_4AlC_3
  - 500°C, 1000 h, [O] < 10^{-10} mass%; $(Nb,Zr)_4AlC_3$, $(Zr,Ti)_3AlC_2$ & $(Zr,Ti)_2AlC$, Zr_3AlC_2, Zr_2AlC



@500°C

CW: cold-worked
SA: solution-annealed

- Depth of dissolution attack:
  - 50-265 µm CW steel
  - 9-125 µm SA steel

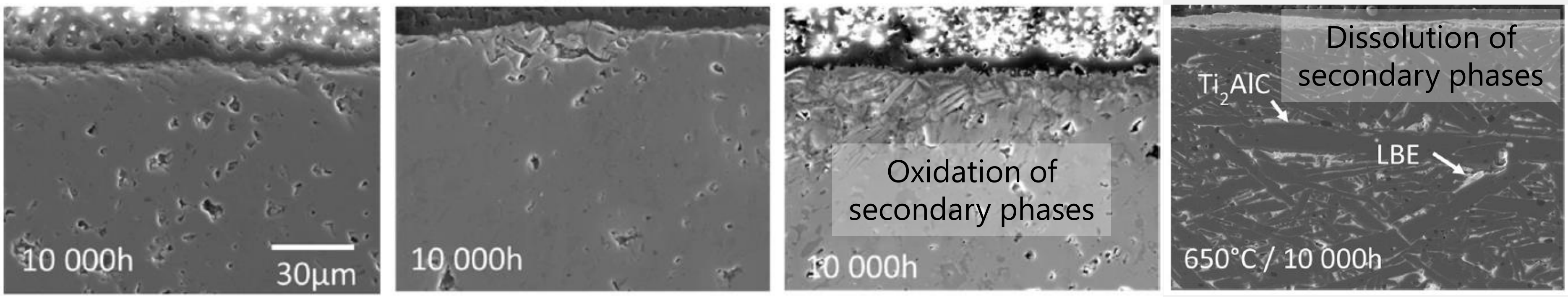
- Depth of dissolution attack:
  - 13-128 µm CW steel
  - 14-48 µm SA steel

STEP 3 Compatibility with Static LBE (LMC)

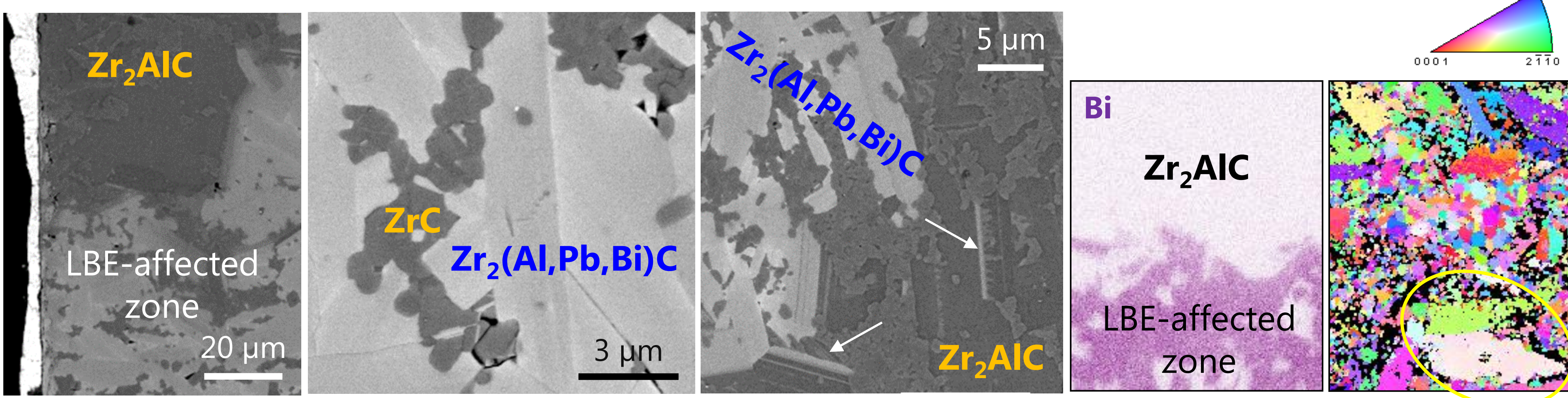
KIT Karlsruher Institut für Technologie

Ti_3SiC_2: 550/650/700°C, static LBE, **10000 h**, [O] ≈ 10^{-8} mass%

Ti_2AlC: 650°C, static LBE, **10000 h**, [O] ≈ 10^{-8} mass%

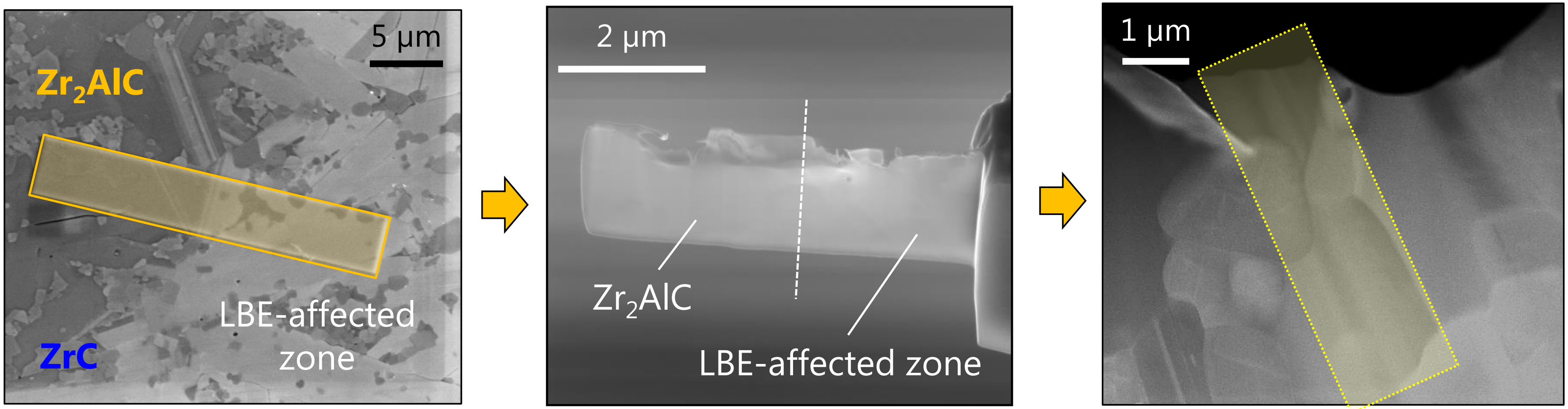


- Specimen maintains its integrity; grain morphology remains unaffected



STEP 3

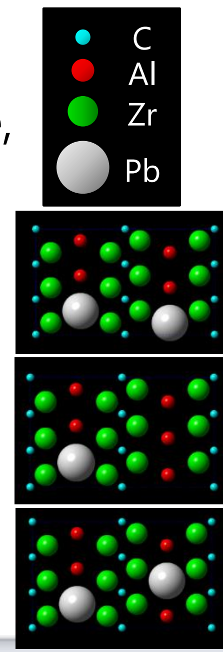
LBE/Zr_2AlC Interaction Mechanism (LMC)

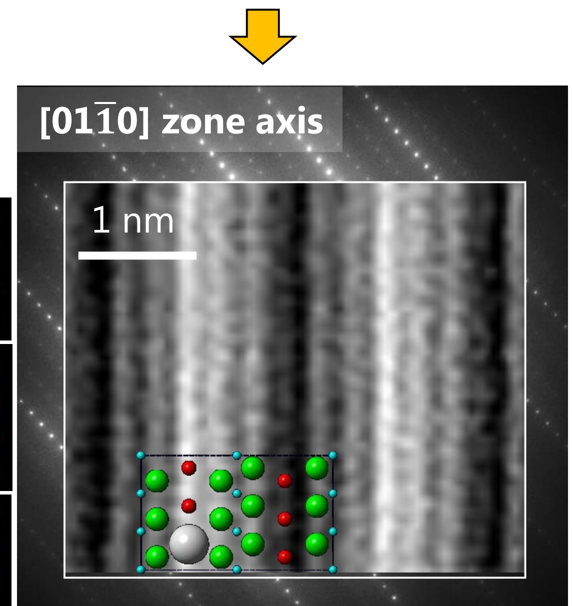


Observations:

- Pb/Bi atoms diffuse along Z... C basal plane, forming *in situ* $Zr_2(Al,P$... solution
- Superlattice reflecti... DP suggest spontaneous ... in crystal lattice
- MAX pha... their initial shape despi... tion (SEM & EBSD data)
- MAX ... ns with mixed contrast show a redu... Al content where Pb/Bi increases (TEM EDS data not shown here)

What happens with mechanical properties after *in situ* formation of $Zr_2(Al,Pb,Bi)C$ solid solution?

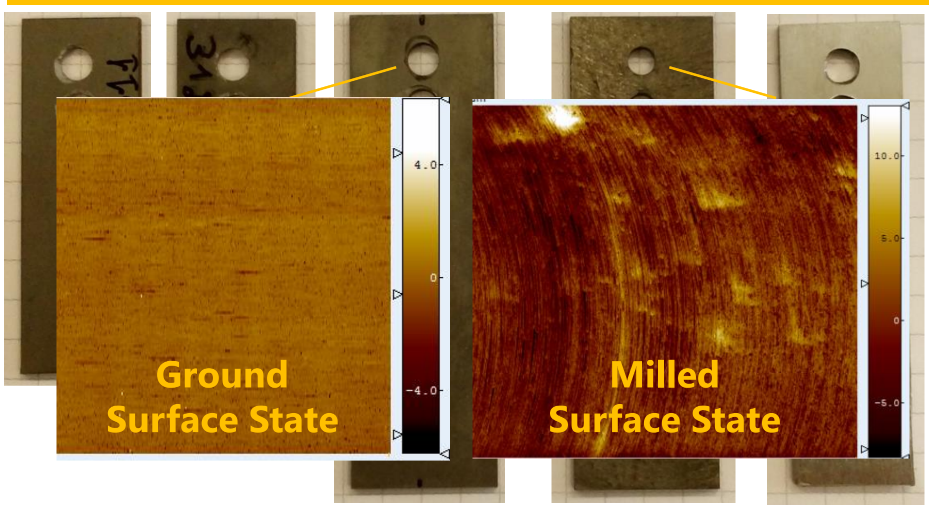




STEP 3 Compatibility with Fast-Flowing LBE (Erosion)

- Test relevant for Gen-IV LFR pump impellers:
  - Materials: Zr_3AlC_2, Zr_2AlC, $(Nb,Zr)_4AlC_3$ ground & milled, 316L steel ground (ref)
  - Test: 500°C, ~1000 h, LBE with [O] < 10^{-10} mass%, v ≈ 8 m/s
- Results: Zr_2AlC & Zr_3AlC_2 broke during removal; profilometry & SEM revealed max erosion damages in 316L steel, min damages in $(Nb,Zr)_4AlC_3$

Zr_2AlC (ZrC)	Zr_3AlC_2 (ZrC)	$(Nb,Zr)_4AlC_3$ Ground	$(Nb,Zr)_4AlC_3$ Milled	316L Ground



Before CORELLA Testing

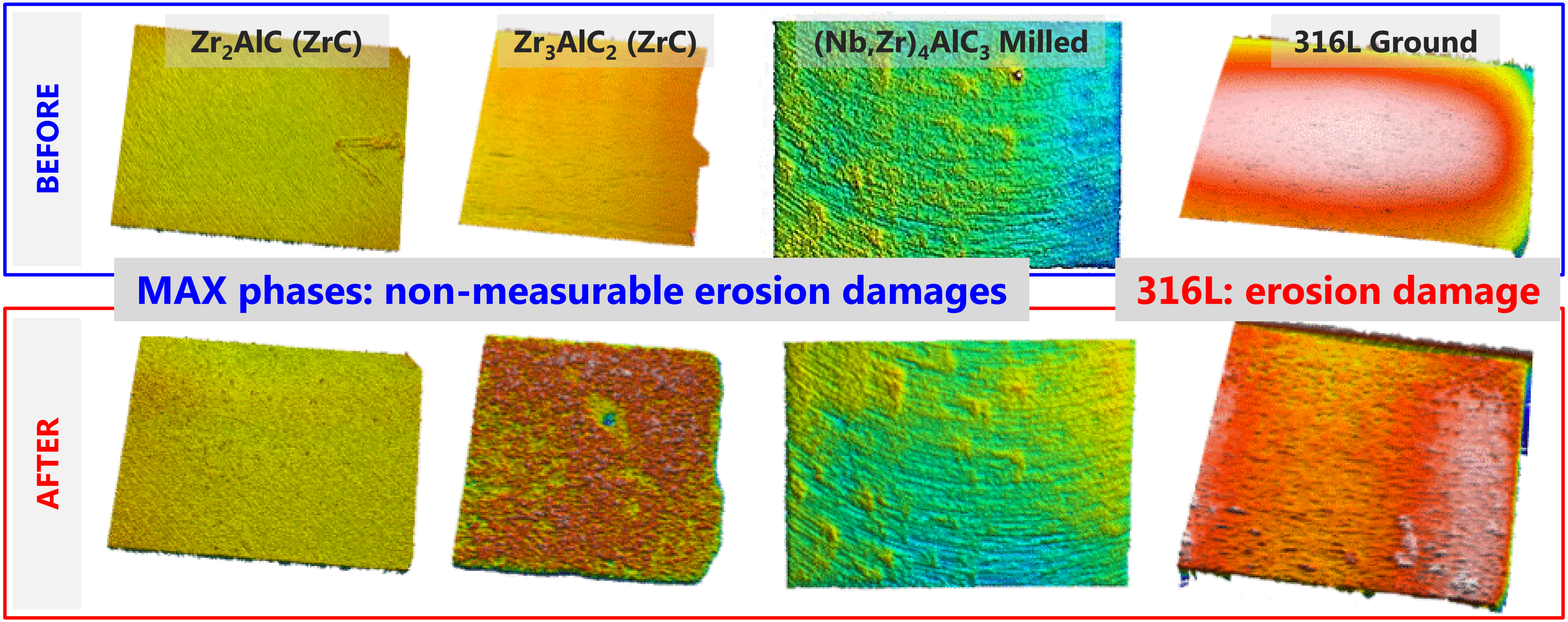
Zr_2AlC (ZrC)	Zr_3AlC_2 (ZrC)	$(Nb,Zr)_4AlC_3$ Ground	$(Nb,Zr)_4AlC_3$ Milled	316L Ground

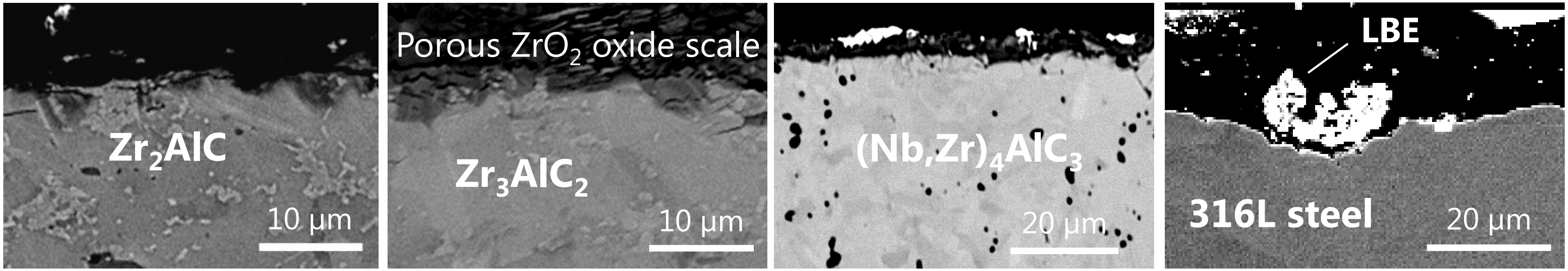
After CORELLA Testing*

* LBE removal: hot oil & etching by 1:1:1 $H_2O_2/C_2H_5OH/CH_3COOH$

STEP 3

Compatibility with Fast-Flowing LBE (Erosion)





MAX Phase R&D: Approach, Challenges, Achievements

Step 1
Production of MAX-phase candidate materials

Step 2
Screening mechanical tests in air on MAX-phase candidate materials

Step 3
Screening liquid metal corrosion / erosion tests on MAX-phase candidate materials

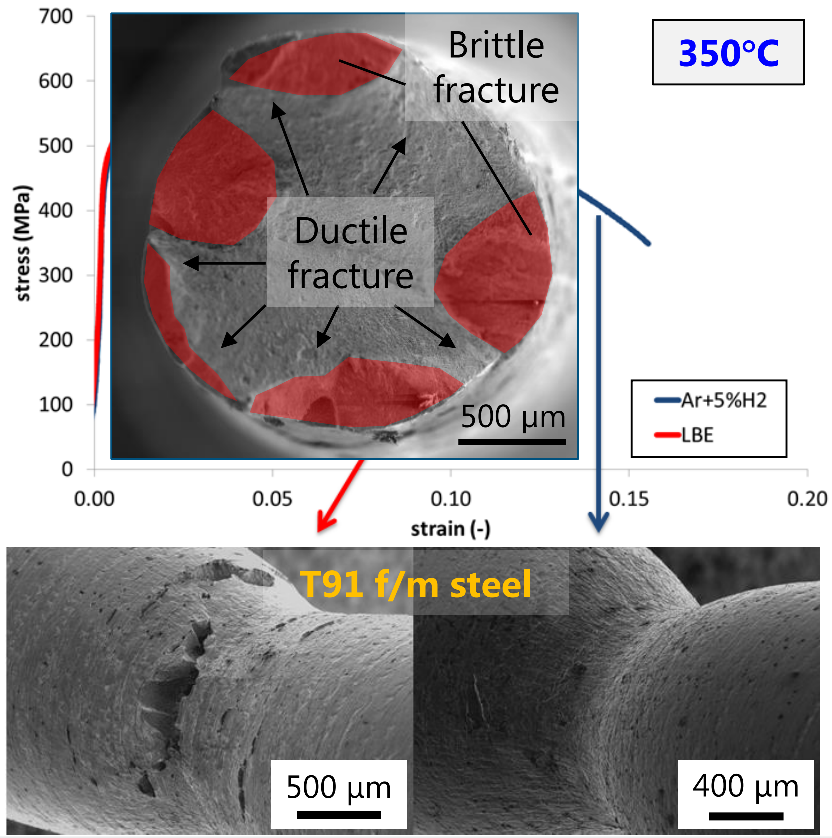
Step 4
Screening mechanical tests in LBE on MAX-phase candidate materials

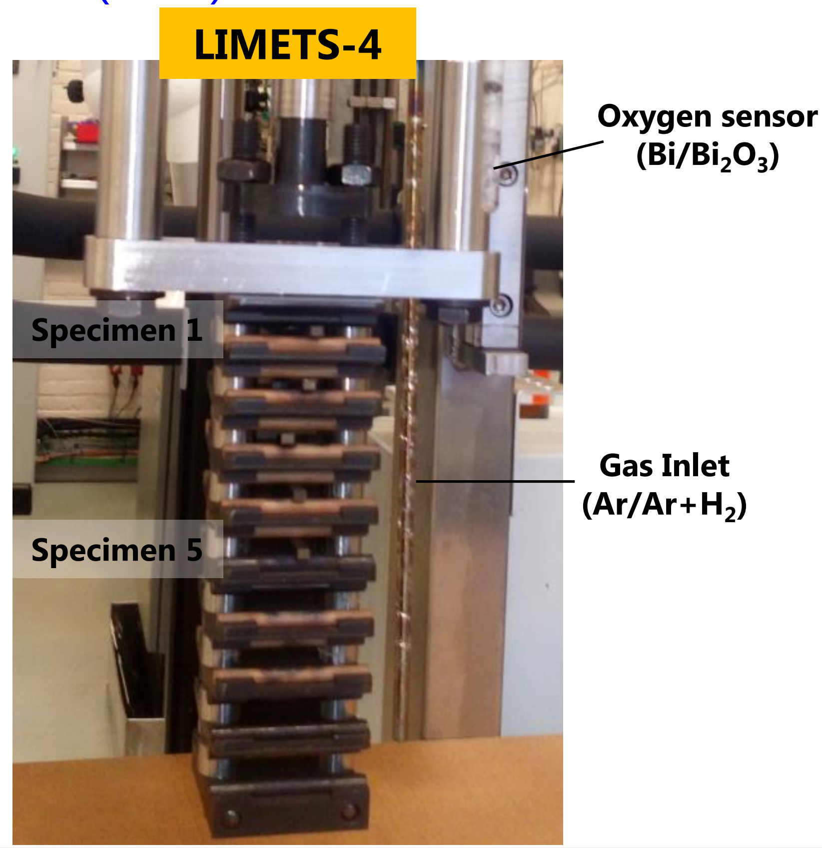
Step 5
Screening irradiation tests

- Step 1 → Step 2, Step 3, Step 4
- Step 2 — not ok → Step 1; ok → Step 3; ok → Step 5
- Step 3 — not ok → Step 1; ok → Step 4; ok → Step 5
- Step 4 — not ok → Step 1; ok → Step 5

STEP 2 STEP 4 Mechanical Properties (Air/Ar+H_2 vs. LBE)

- Aim: assess whether the exposure of MAX phases to liquid LBE affects their mechanical properties (flexural strength, fracture toughness)
- Example of materials degradation observed in ferritic/martensitic steels in contact with LBE: liquid metal embrittlement (LME)





(*Courtesy: G. Coen & S. Gavrilov)

STEP 2 STEP 4

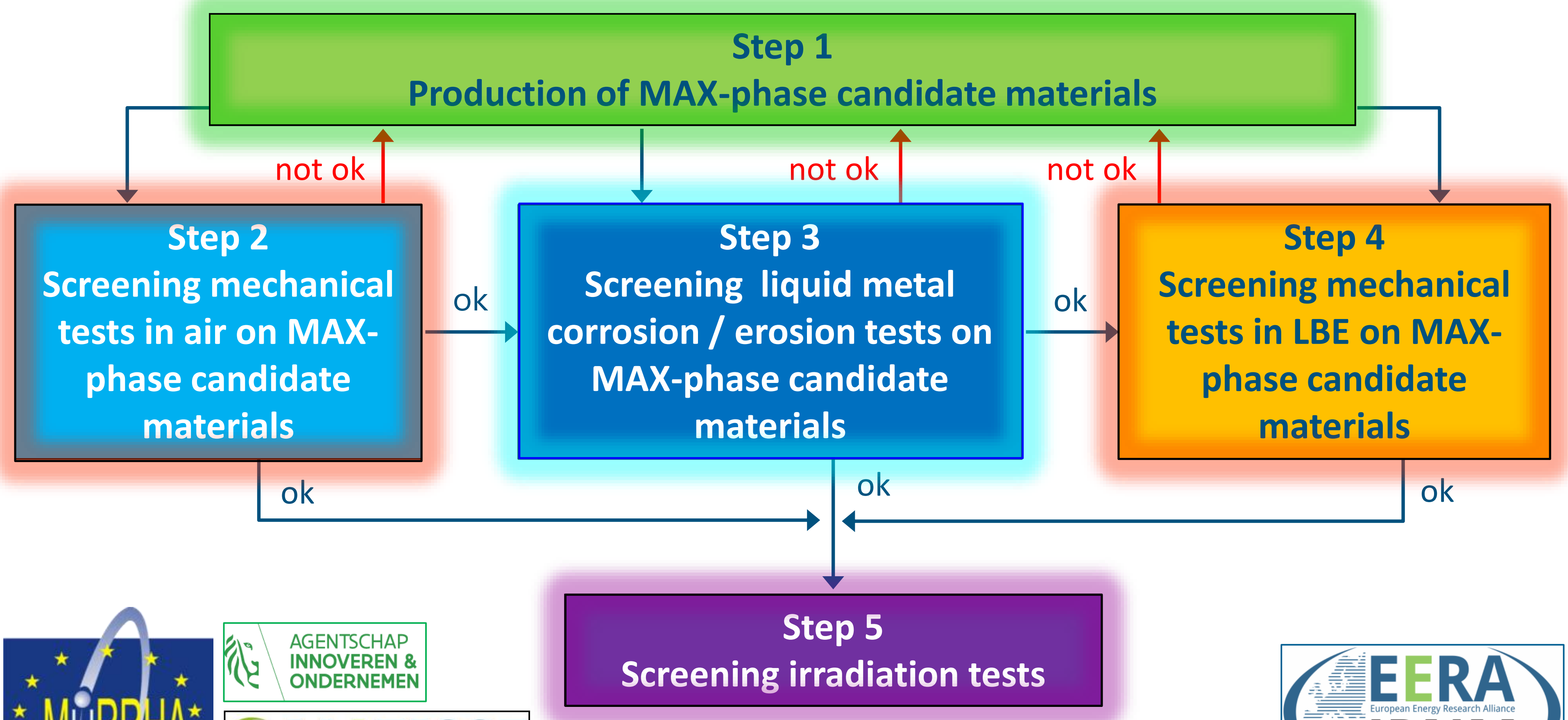
4PB Strength (Air/Ar+H_2 vs. LBE)

- Evaluation of four point-bending strength (σ_{4PB}) in LIMETS-4
- σ_{4PB} is given as an average of 5 tests per material and condition
  - Materials: Maxthal 211® and $(Nb_{0.85},Zr_{0.15})_4AlC_3$
  - Test Conditions & Methodology:
    - room temperature (RT) in air (T monitored by thermocouple)
    - 350°C in Ar-5 vol% H_2 (T monitored by thermocouple)
    - 350°C* in LBE with [O] < 10^{-10} mass% (T & [O] monitored – oxygen sensor)
    - Specimen pre-exposure: 48 hours under 20 MPa in test environment
- Results: no environmental degradation of MAX phase flexural strength!

	Maxthal 211®	$(Nb_{0.85},Zr_{0.15})_4AlC_3$
Test Condition	**σ_{4PB} (MPa)**	**σ_{4PB} (MPa)**
RT in air	204 ± 17	426 ± 30
350°C in Ar-5% H_2	197 ± 10	418 ± 60
350°C in LBE with [O] < 10^{-10} mass%	214 ± 13	414 ± 56

* **350°C:** most severe LME in ferritic/martensitic steels

MAX Phase R&D: Approach, Challenges, Achievements



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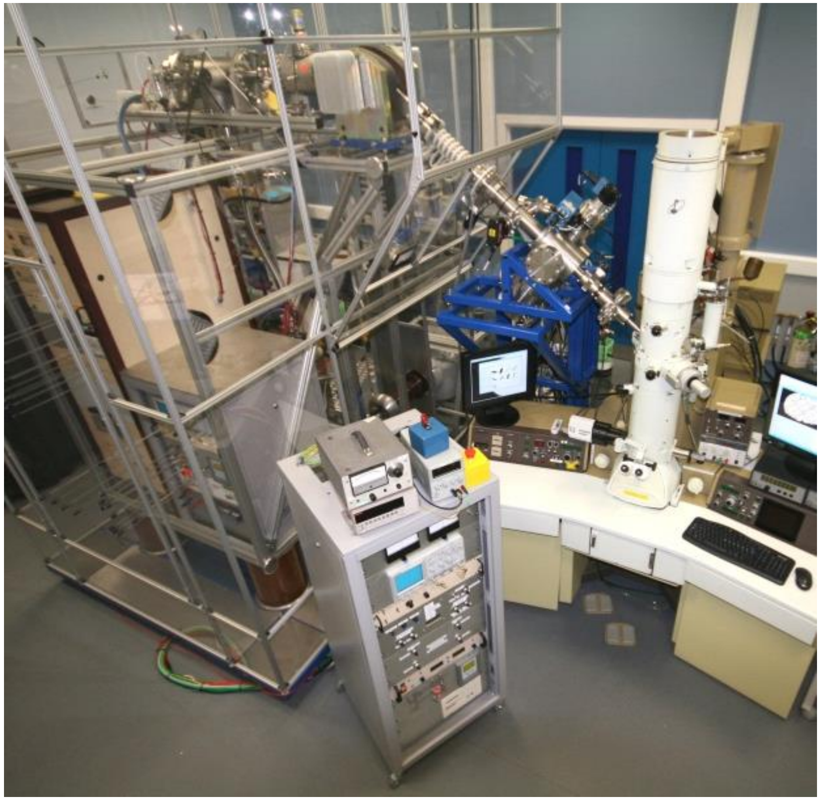
STEP 5

Ion Irradiation of $(Nb_{0.85},Zr_{0.15})_4AlC_3$

Microscope and Ion Accelerator for Materials Investigations (MIAMI-1) Facility

Specifications	
TEM	JEOL JEM-2000FX
Electron acceleration voltage	80 to 200 kV
Ion acceleration voltage	1 to 100 kV
Ion species	Most ions from H^+ to W^+
Electron/ion beam angle	30°
Ion flux	Up to 1.5×10^{14} ions cm^{-2} s^{-1} for 6 keV He^+ (for example)
Temperature	(100 to 380 K) or (RT to 1570 K)
Image capture	Gatan ES500W & Gatan Orius SC200 (4 MP)



EPSRC Engineering and Physical Sciences Research Council

University of HUDDERSFIELD

STEP 5

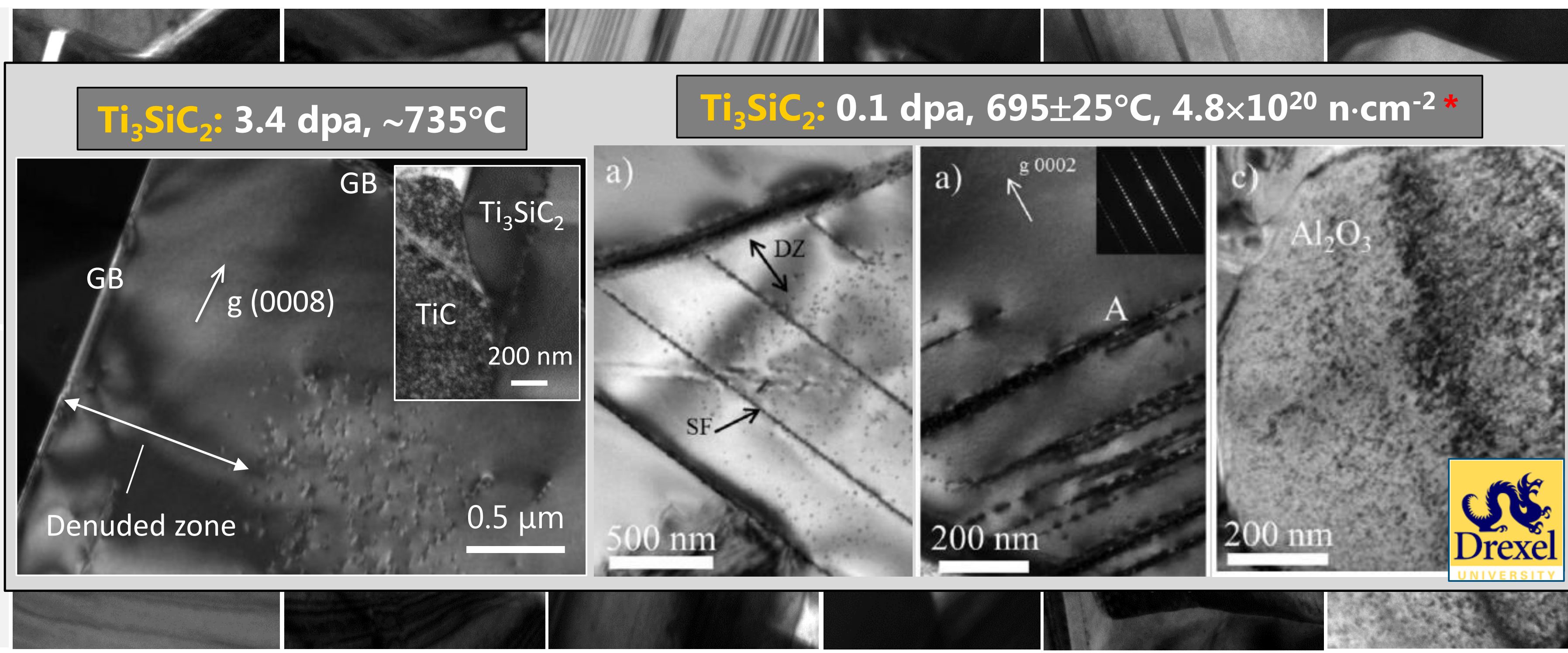
Ion Irradiation of $(Nb_{0.85},Zr_{0.15})_4AlC_3$

- Irradiation with 6 keV He^+; ion flux: 10^{14} ions·cm^{-2}·s^{-1}
- Electron beam energy: 200 keV; electron beam: off during ion irradiation

	20°C		350°C		600°C	
	MAX Phase	Secondary Phases*	MAX Phase	Secondary Phases*	MAX Phase	Secondary Phases*

0 dpa, 0 ions·cm^{-2}

10 dpa, 2.1×10^{17} ions·cm^{-2}



500 nm

(*D. Tallman et al., *J. Nucl. Mater.* **468** (2016) 1–13)

*Al_3Nb (7 wt%) & Al_2O_3 (2-3 wt%)

Conclusions

- Exploring the potential of MAX phases for specific applications *(fuel clads, impellers)* in Gen-IV LFRs & MYRRHA entails the following challenges:

  i. Strict control of processing to produce phase-pure materials with a tailored microstructure that meet the targeted property requirements (strength, fracture toughness, fatigue lifetime) of the end application

  ii. Assess the compatibility of produced materials with the heavy liquid metal coolant (Pb, LBE) under variable exposure conditions (T, [O], flow velocity) – study liquid metal corrosion/erosion behavior of candidate materials

  iii. Measure key mechanical properties (strength, fracture toughness) of produced materials both in air/inert and heavy liquid metal media to assess possible susceptibility to environment-assisted material degradation effects (e.g., LME)

  iv. Assess the radiation tolerance of the optimized materials by designing and executing neutron irradiation campaigns that can validate the materials in an industrially-relevant environment (TRL 5). Ion/proton irradiation – when used in the right way – will help to accelerate development of radiation-tolerant MAX phase materials prior to their ultimate validation in neutrons

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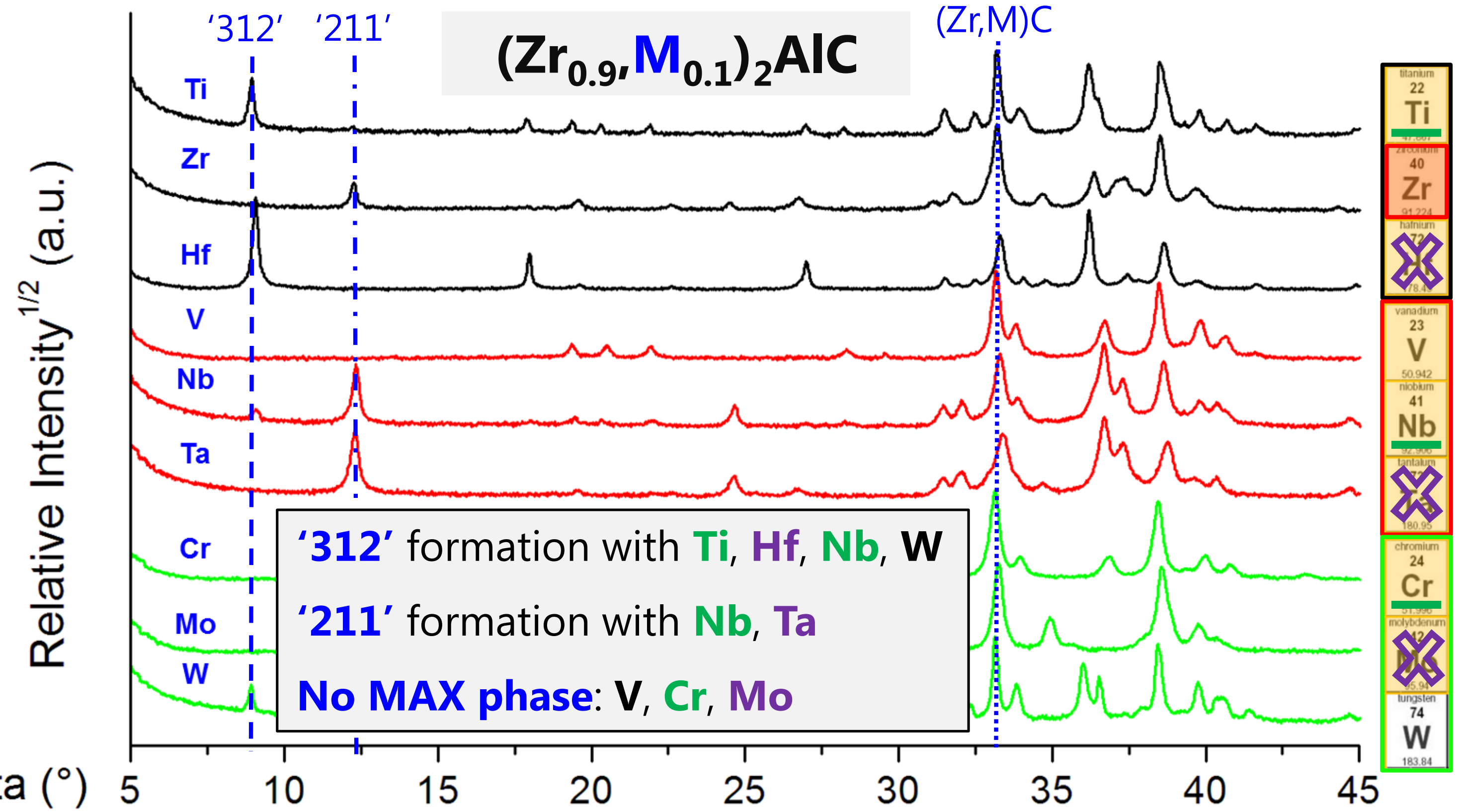
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

MAX Phase Synthesis in the (Zr,M)-Al-C System

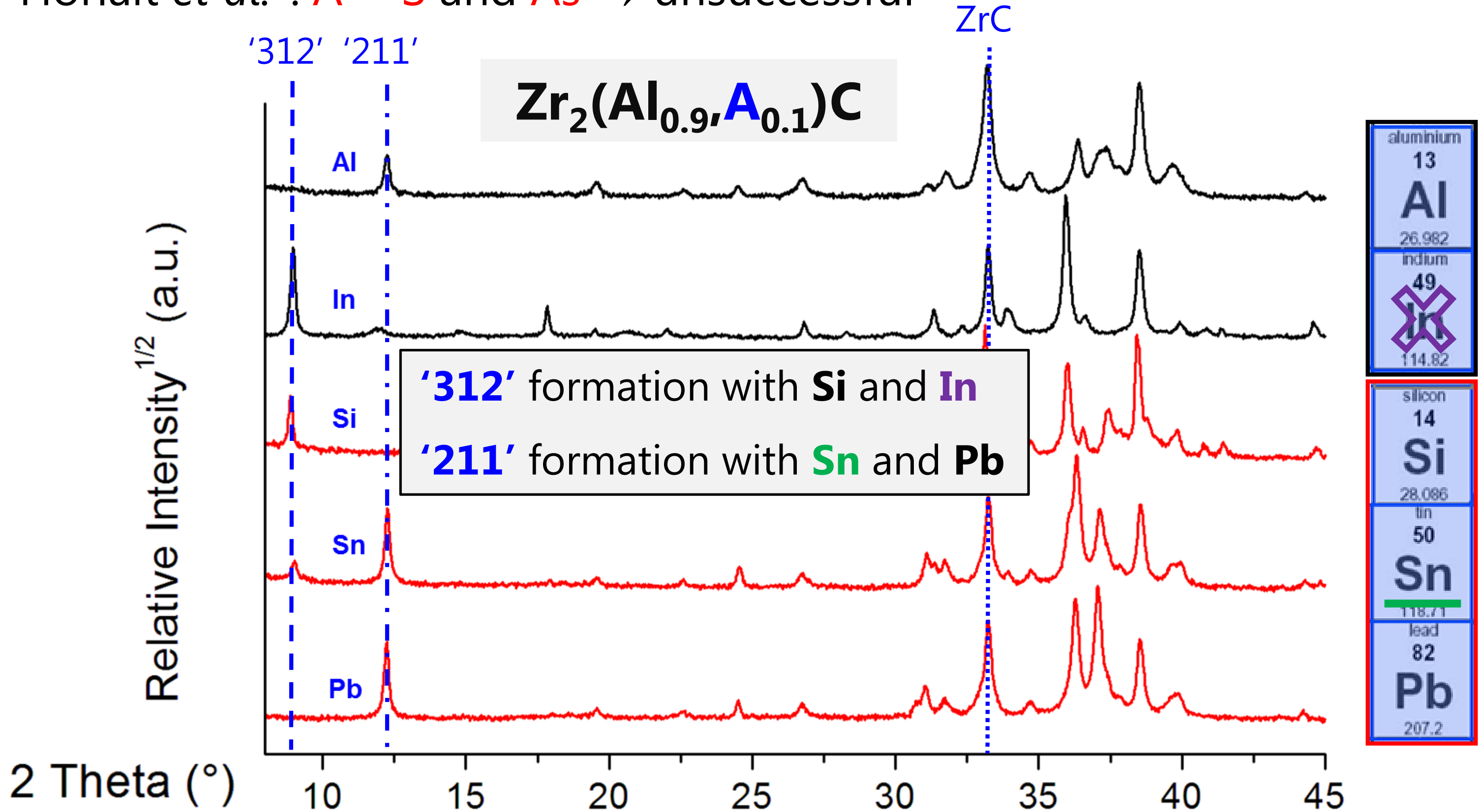
- Aim: synthesize $(Zr_{1-x},M_x)_2AlC$ solid solutions to increase MAX phase content
- Prior attempts reported in literature:
  - Reiffenstein *et al.*[1] & Naguib *et al.*[2]: M = Nb → successful for x = 0.6 & 0.8 resp.
  - Horlait *et al.*[3]: M = Ti, Cr and Mo → unsuccessful



[1] *Monatsh. Chem.* **97** (1966) 1427; [2] *Mater. Res. Lett.* **2** (2014) 233-240; [3] *Mater. Res. Lett.* **4** (2016) 137–144

MAX Phase Synthesis in the Zr-(Al,A)-C System

- Aim: synthesize $Zr_2(Al_{1-x},A_x)C$ solid solutions to increase MAX phase content
- Prior attempts reported in literature:
  - Horlait *et al.*[1,2]: A = Sn, Pb, Sb & Bi → successful for x = 0.8, 0.65, 0.7 & 0.58 resp.
  - Horlait *et al.*[1]: A = S and As → unsuccessful

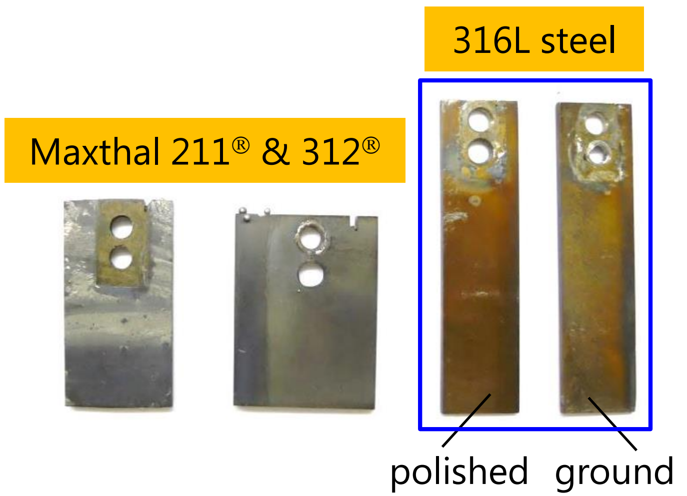


[1] *Mater. Res. Lett.* **4** (2016) 137–144 ; [2] *Scientific Reports* **6** (2016) 18829

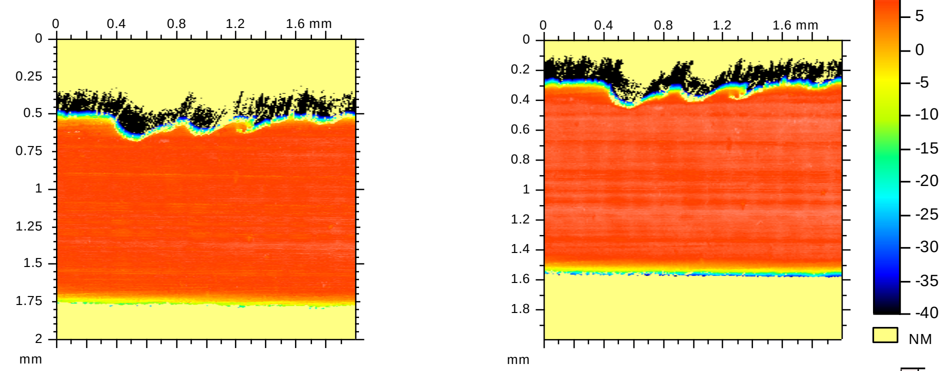
CORELLA Test Results

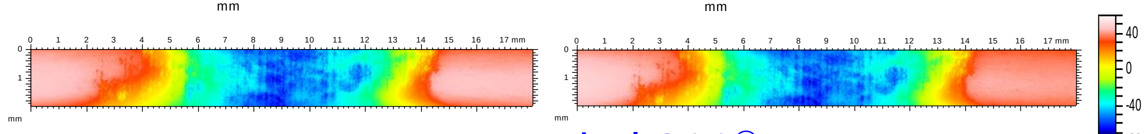
- Tests relevant for MYRRHA pump impeller:
  - Materials: Maxthal 211® & 312®, 316L stainless steel ground & polished
    - 1st test: 300°C, 500 h, LBE with [O] < 10^{-8} mass%, v ≈ 8 m/s
    - 2nd test: 300°C, 500 h, LBE with [O] ≈ 10^{-6} – 10^{-5} mass%, v ≈ 8 m/s
    - 3rd test: 300°C, 1000 h, LBE with [O] ≈ 10^{-7} mass%, v ≈ 8 m/s
- Results: no clear evidence of erosion damage; possible local damages in 316L steel and Maxthal 211® – difficult interpretation

SPECIMENS AFTER 2ND TEST



Side: 316L ground





Front: Maxthal 211®