Liquid Metal coolants for high power heat transport systems

P. Hosemann,

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SunShot
U.S. Department of Energy

OUTLINE

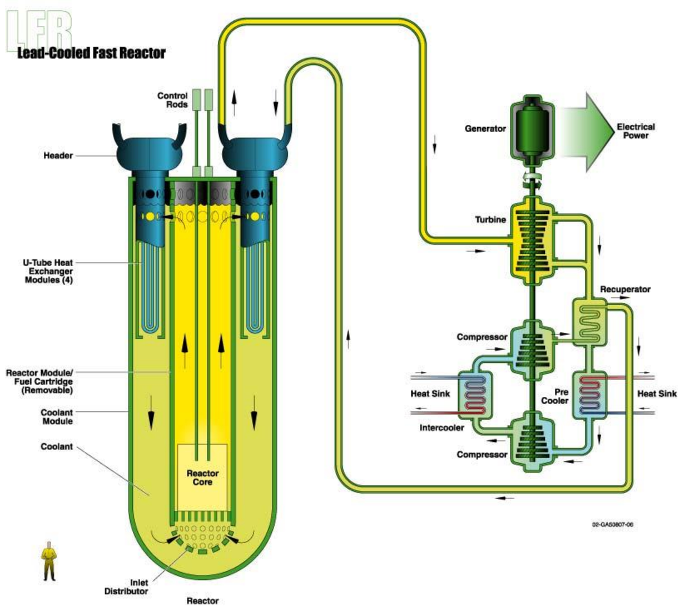
- Introduction; Engineering applications utilizing liquid metals.
- Introduction; Selected issues using heavy liquid metals.
- Results on stainless steel in static and flowing Lead Bismuth Eutectic at medium temperature
- Results of Fe-Cr-Al steels in flowing and static LM at medium and high temperature.
- Evaluating the adhesion of oxides on the substrate.
- Experimental approach on evaluating the effects of radiation on corrosion.
- Summary

Why Liquid metal technology

Issues with liquid metal technology

LIQUID METAL COOLED POWER SYSTEMS

NUCLEAR FISSION POWER



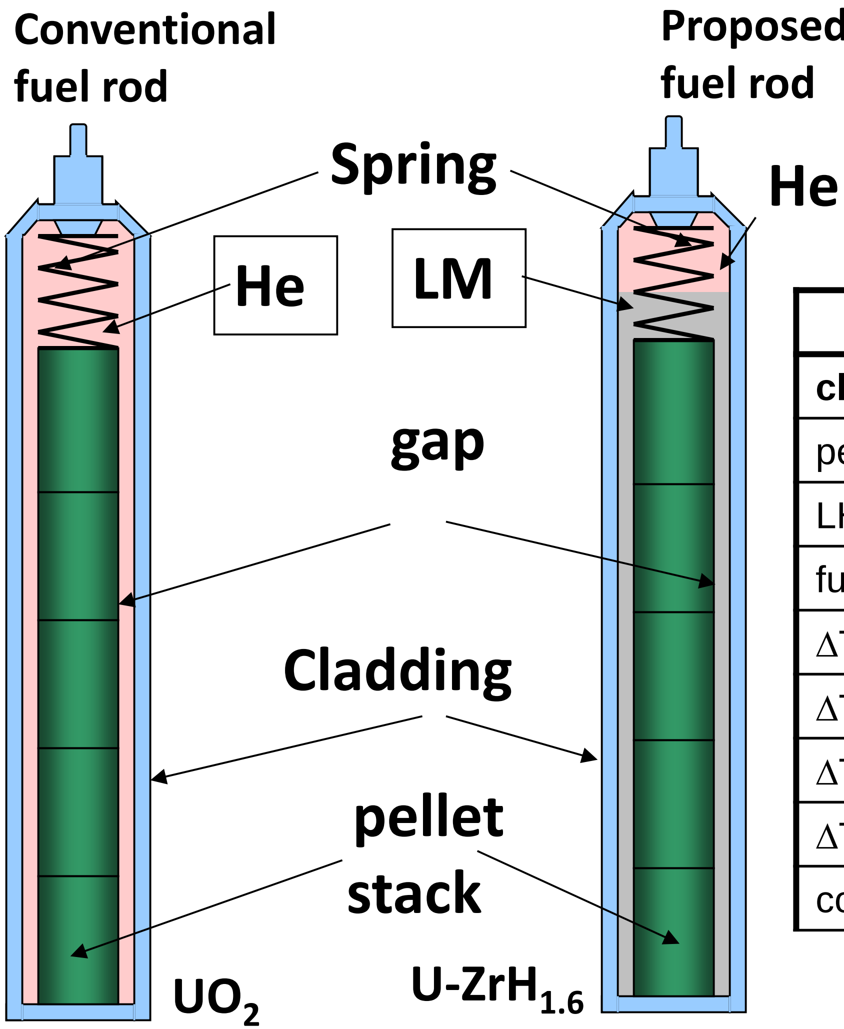
- Fast neutrons
- High neutron yield in ADS or spallation sources
- Good thermal properties
- Low melting point
- High boiling point
- Cost effective
- Low viscosity

SOLAR CONCENTRATING POWER (CSP)

- Good thermal properties
- Low melting point
- High boiling point
- Costs effective
- Low viscosity

LM AS FILLER FOR FUEL RODS

Conventional UO_2 and He gap have limited thermal properties leading to very high temperatures in the fuel centerline.
Other fuel concepts might be considered bypassing some of these issues.

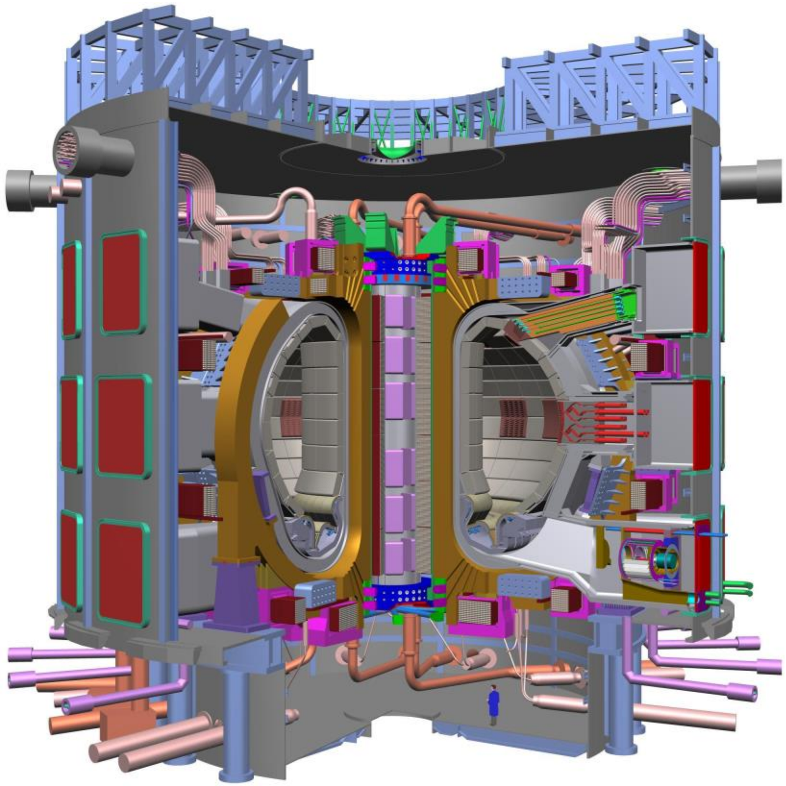


	hydride	hydride	oxide
characteristic	**He bond**	**LM bond**	**He bond**
pellet OD, mm	10	10	10
LHR, W/cm	**375**	**375**	**375**
fuel centerline, °C	680	**555**	1505
ΔT_{fuel}	170	170	995
ΔT_{gap} (35 μm) °C	125	**1**	125
ΔT_{clad} °C	46	46	46
ΔT_{fluid} °C	39	39	39
coolant, °C	300	300	300

D. Olander, M. Balooch, K. Terrani, P. Hosemann

OTHER LIQUID METAL APPLICATIONS

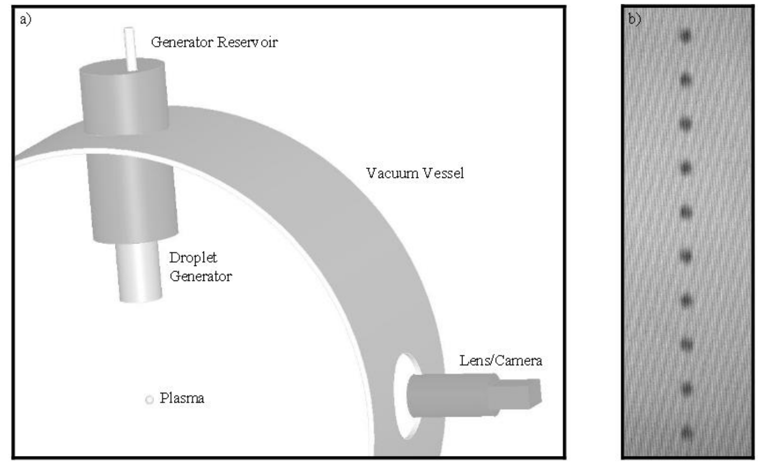
NUCLEAR FUSION POWER



Good thermal properties
Low melting point
High boiling point
Fire hazard of Li can be reduced
Tritium breeding
→ *See Konys talk*

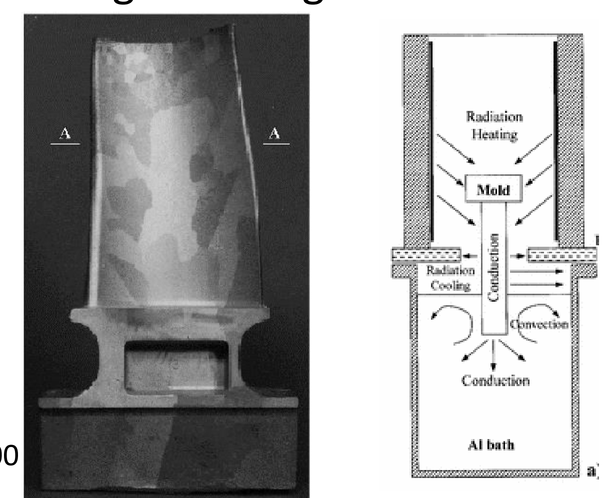
ADDITIONAL TECHNOLOGICAL APPLICATIONS OF LIQUID METALS

Liquid metal used to obtain plasma for EUV light



AJ. M. Algots lithography 2005

Well controlled cooling rate for gas turbine blades



A. Kermanpur MSE-B 2000

LIQUID METALS IN NUCLEAR APPLICATIONS

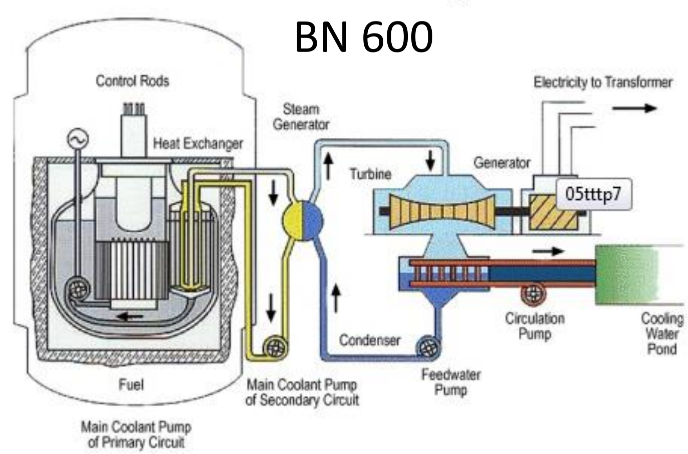
LM's in nuclear applications have been well established.

Clementine reactor first fast reactor
1946-1949 Los Alamos,
Mercury cooled 25kW

Staring in the ***50's*** several liquid lead bismuth cooled submarines were build and commissioned

Several sodium cooled reactors have been realized

BN 600



WHY NEW CSP HEAT TRANSPORT FLUIDS?

- Power transported in CSP is **f(T,cp,V/t)**
- Hydrogen production and process heat generation requires high temperatures.
- High temperatures and high c_p allow for thermal storage over night.

→ *Push the temperature, of the solar concentrator units to >700C!*

New heat transport fluids are required and proposed

Liquid Salt currently temp limited
100 - 550°C nitrate salts
Fluoride salts 450 - 1000C

Liquid metal
100C ->1000C

Many liquid metals have a low melting point

Liquid metals have excellent heat conduction

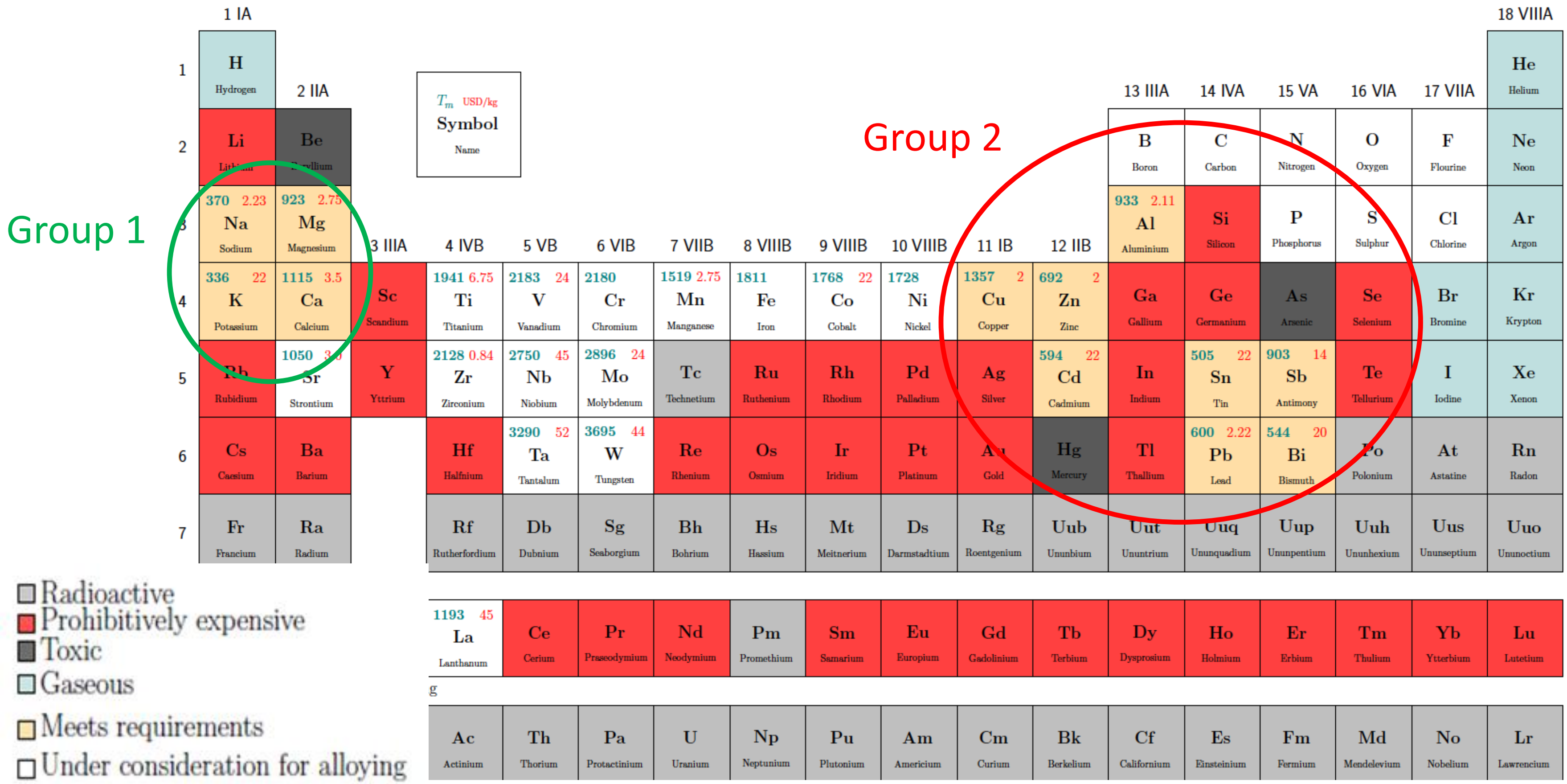
Liquid metals have low viscosity

Many decades of experience with various liquid metals for other applications.

→ Large facilities have been build and successfully operated in the past

REVIEW OF POSSIBLE ELEMENTS FOR LM IN CSP

Melting point, cost, toxicity, boiling points



Based on cost, melting temperature and non-toxicity:

Na, K, Mg, Ca, Cu, Zn, Al, Sn, Pb, Sb, Bi

Melting point below 350°C

Melting point above 350°C

LIGHT AND HEAVY LIQUID METALS

Group 1 light elements:

Large scale facilities have been realized. **(Na)**
Low melting point.
Little corrosion issues

High vapor pressure at high temperatures.
REACTIVE!

Almeria solar plant accident, Spain!!

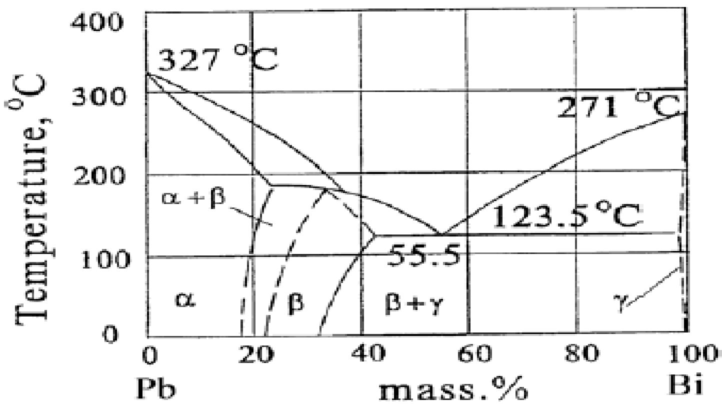
Group 2 heavy elements:

Large scale facilities have been realized
Low melting point (with alloying)
Not reactive with water
Low vapor pressure

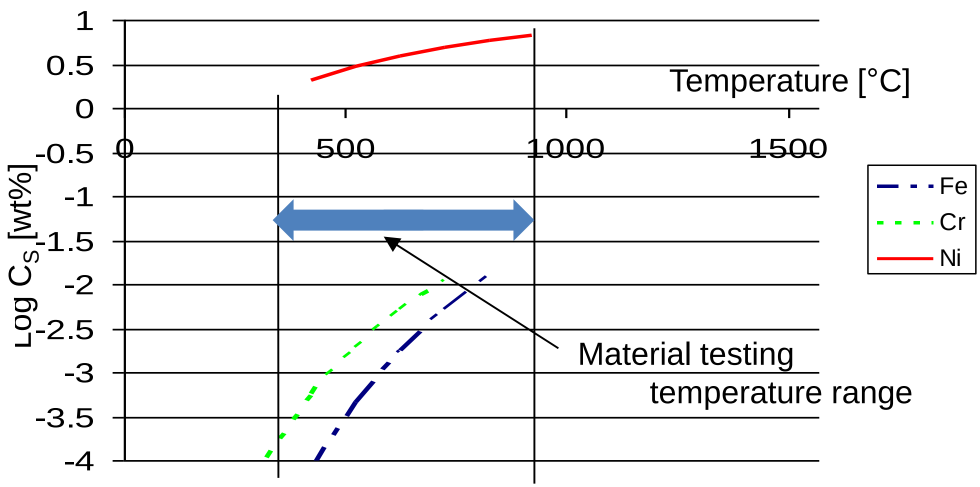
Corrosion issues exist!!

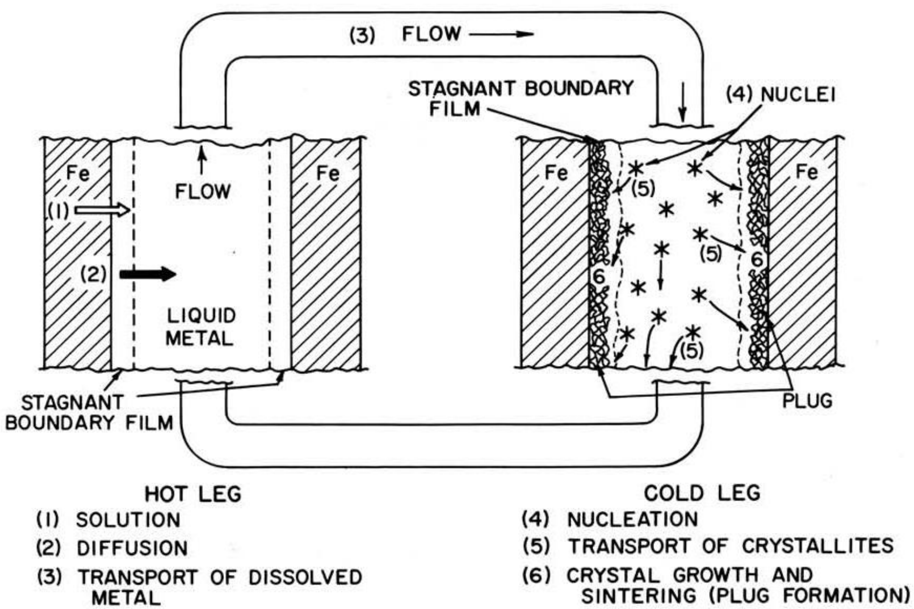
Russian alpha class submarines;
MHYRRA reactor Belgium

WHAT ARE THE CORROSION ISSUES IN HEAVY METALS (EXAMPLE LBE)? DISSOLUTION



Many metals have a solubility in many heavy liquids. In loop systems, this leads to enhance and uncontrolled corrosion if steps are not taken to prevent it.

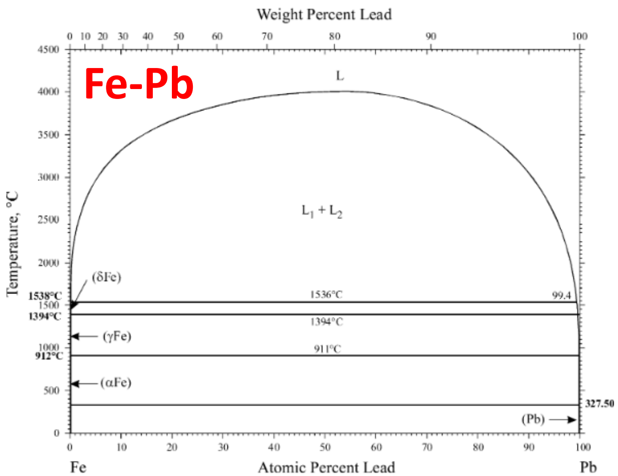


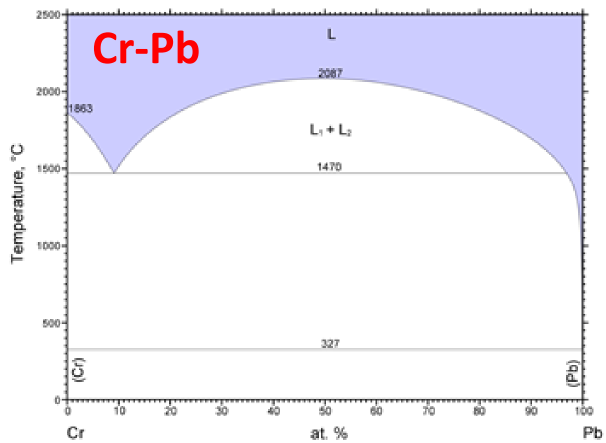


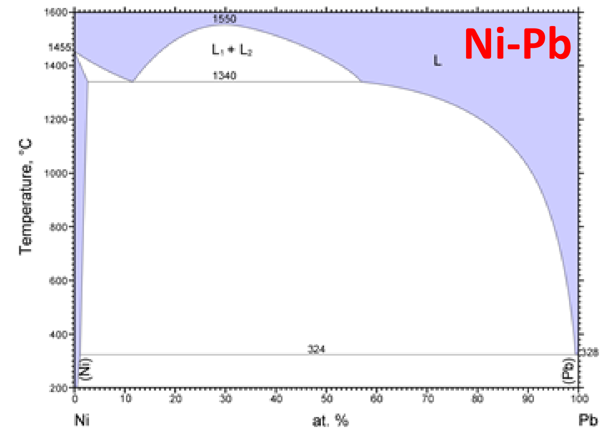
Loop saturated with corrosion products cannot work due to the temperature gradient in the loop!

WHAT ARE THE CORROSION ISSUES IN HEAVY METALS ?
FORMATION OF NEW PHASES

Fe-Cr-Ni in Pb and Bi



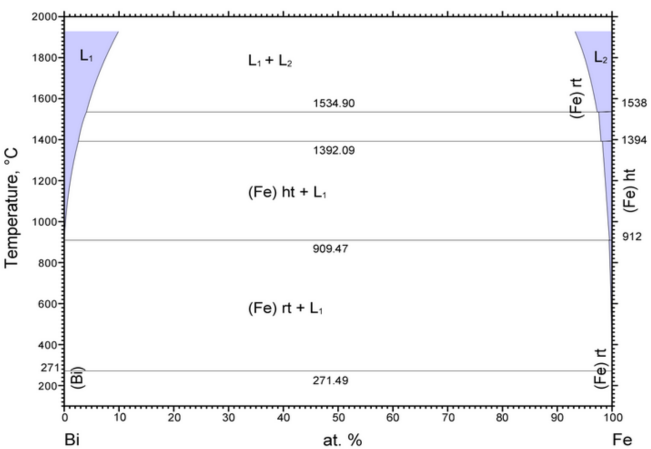




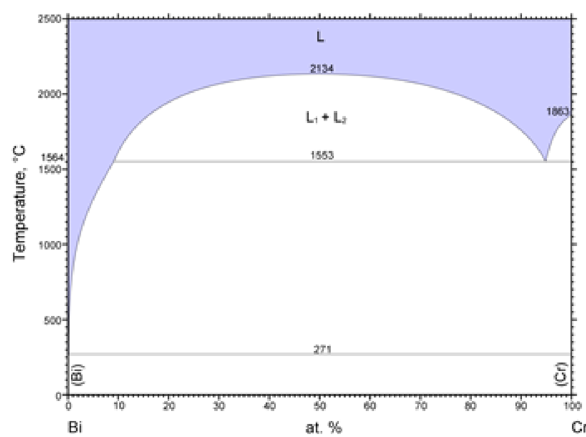
Pb and Bi form few intermetallic phases with steel elements

→ only solubility issues

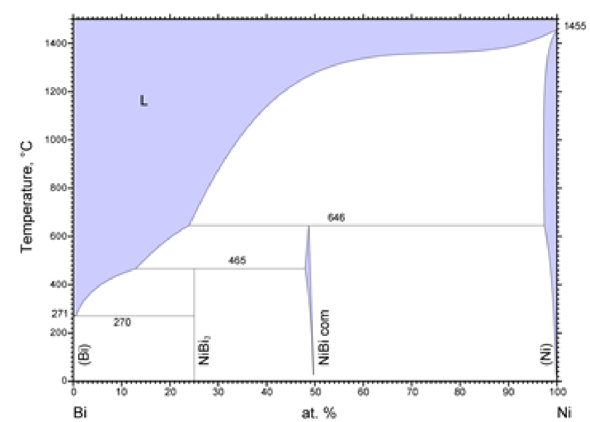
Fe-Bi



Cr-Bi

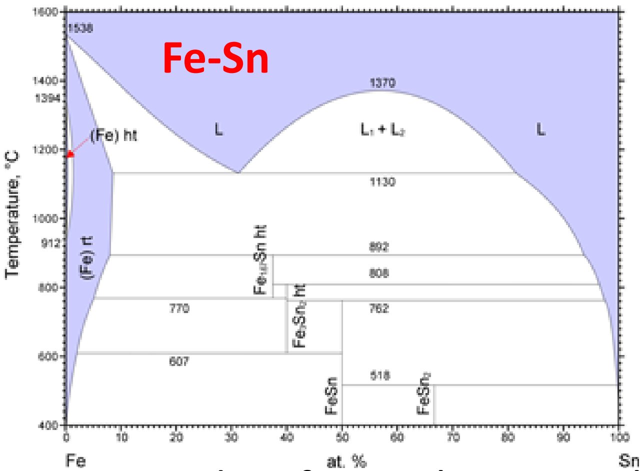


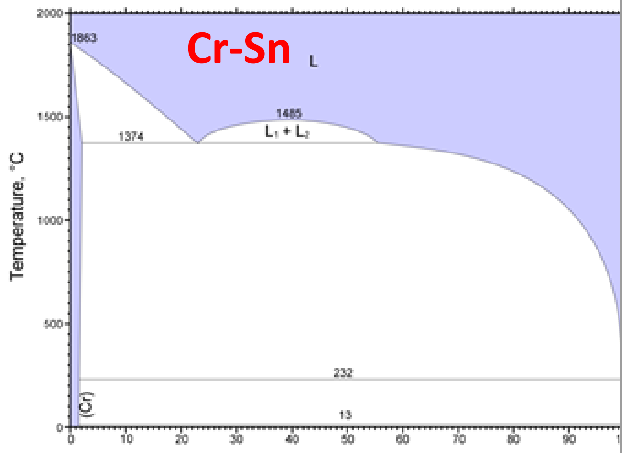
Ni-Bi

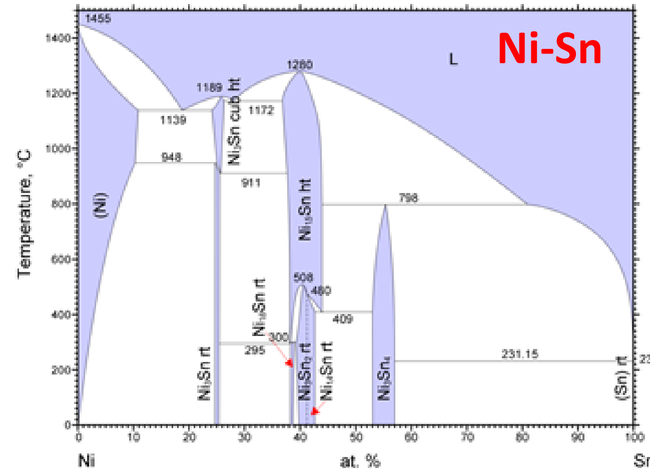


ASM phase diagram database

WHAT ARE THE CORROSION ISSUES IN HEAVY METALS ?
FORMATION OF NEW PHASES



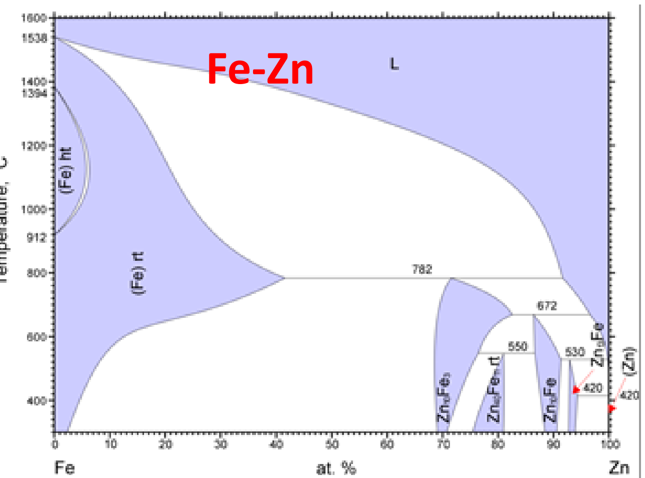


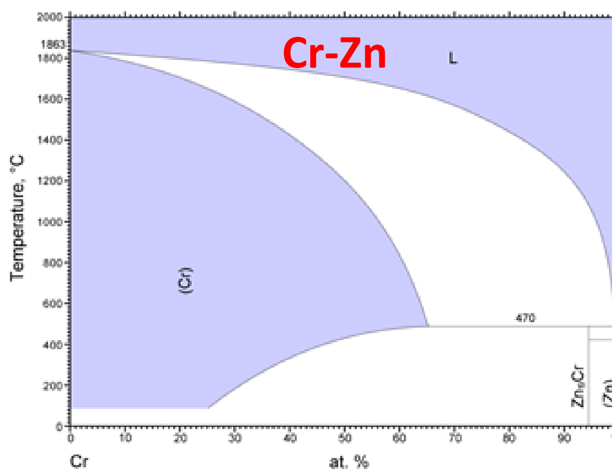


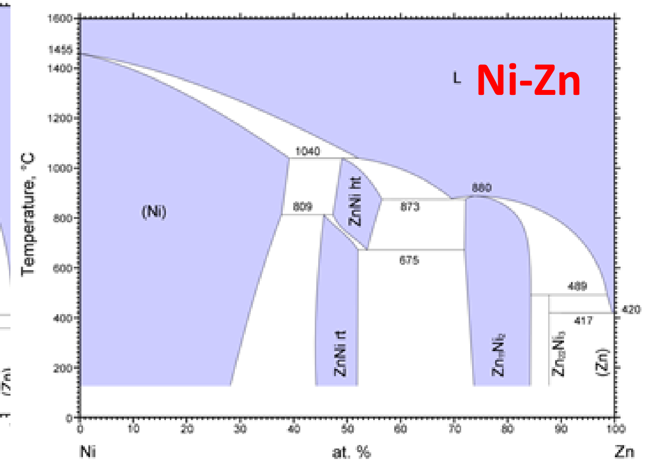
Sn and Zn form a large number of intermetallic phases

→ High corrosion rates may be anticipated

→ danger of clogging due to high temp melting phases

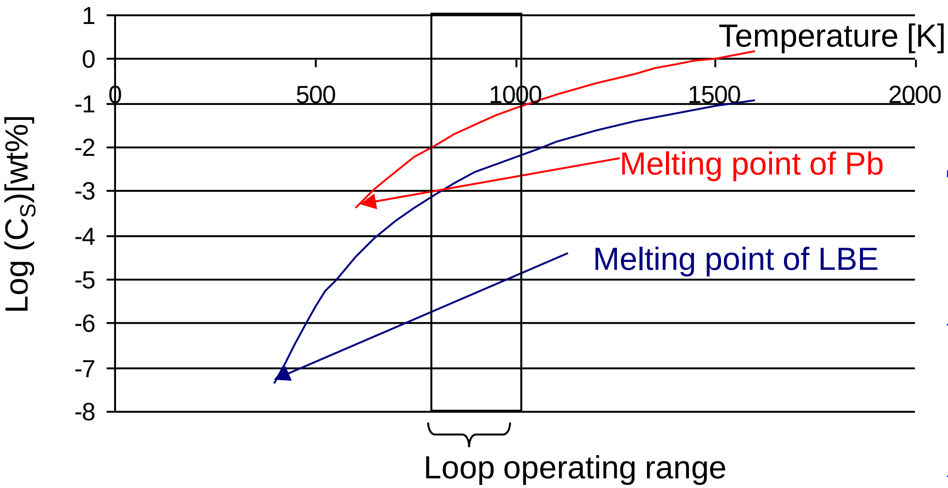




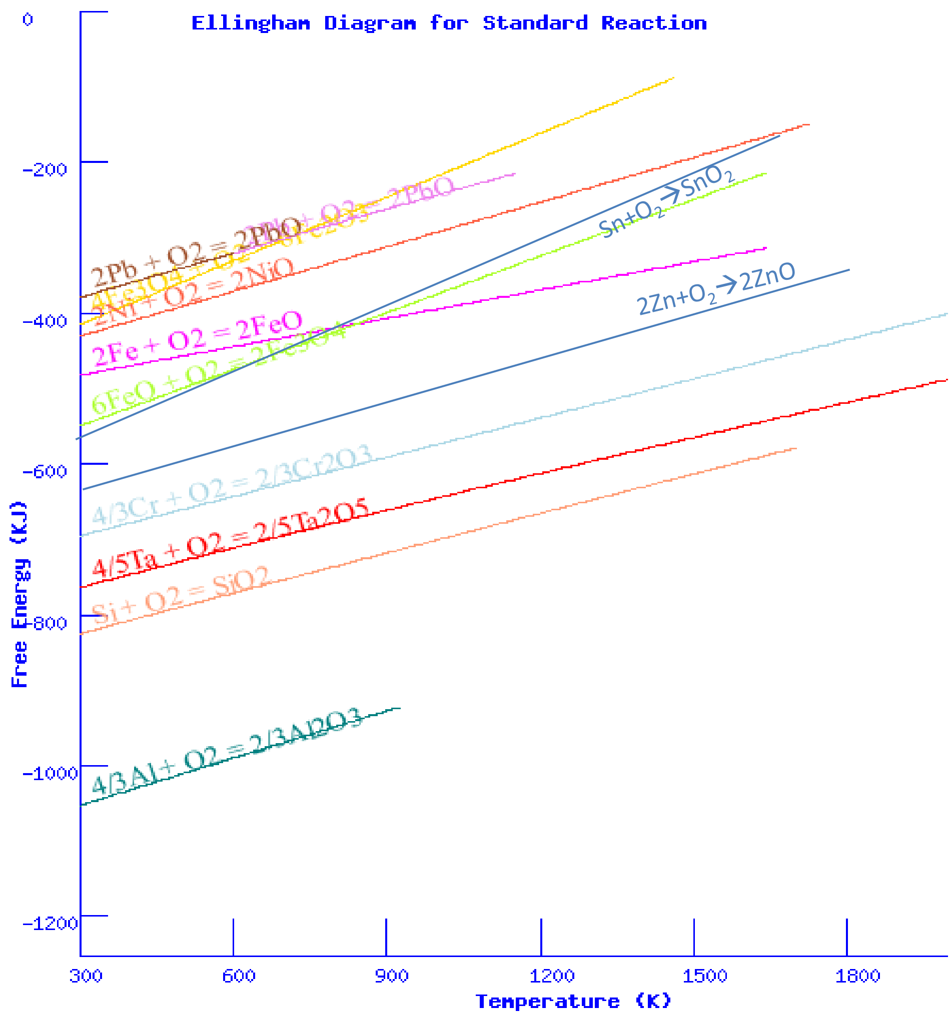


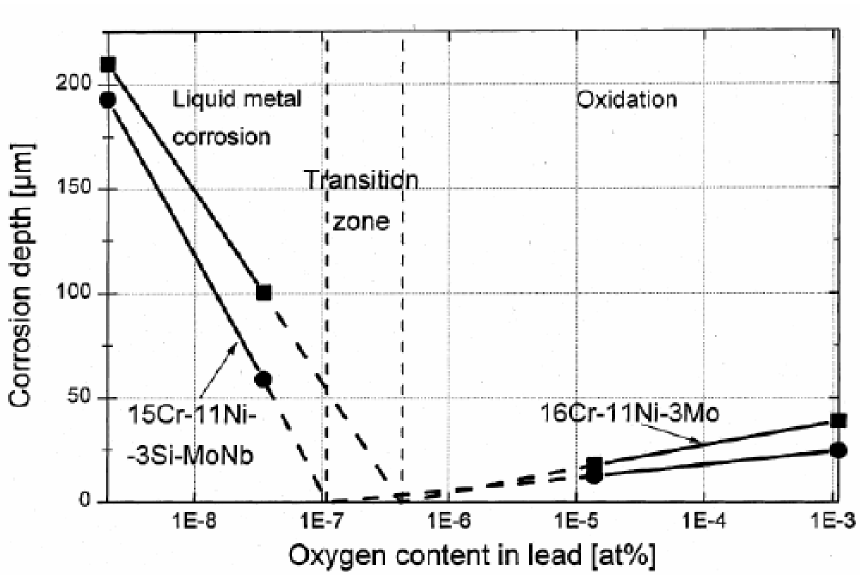
ASM phase diagram database

CORROSION MITIGATION STRATEGY

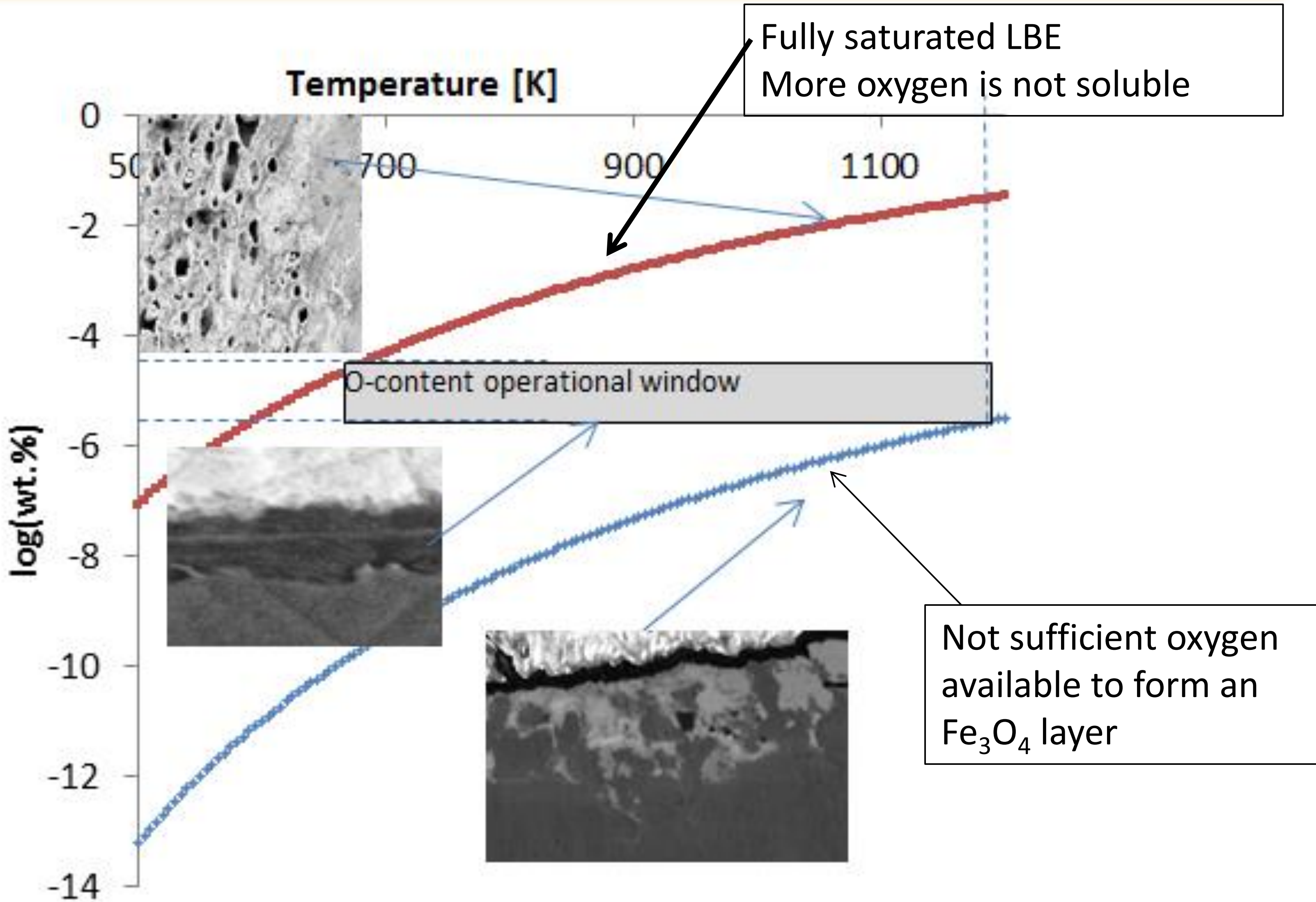


Addition of oxygen allows the formation of a protective film





CONSIDERATIONS FOR OPTIMAL OXYGEN CONTENT



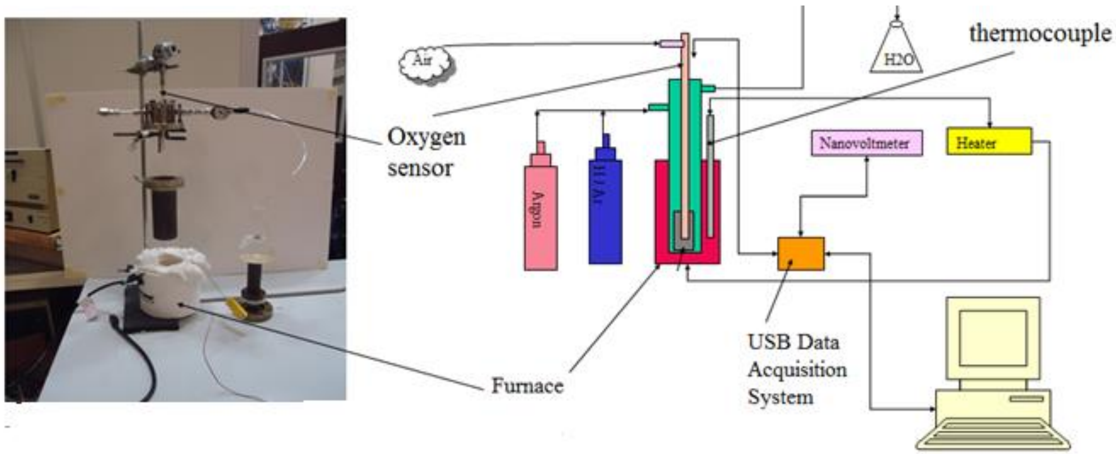
D. Frazer, E. Stergar, C. Cionea, P. Hosemann; SolarPACES 2013, *energy procedia*

Detailed experiments in LBE

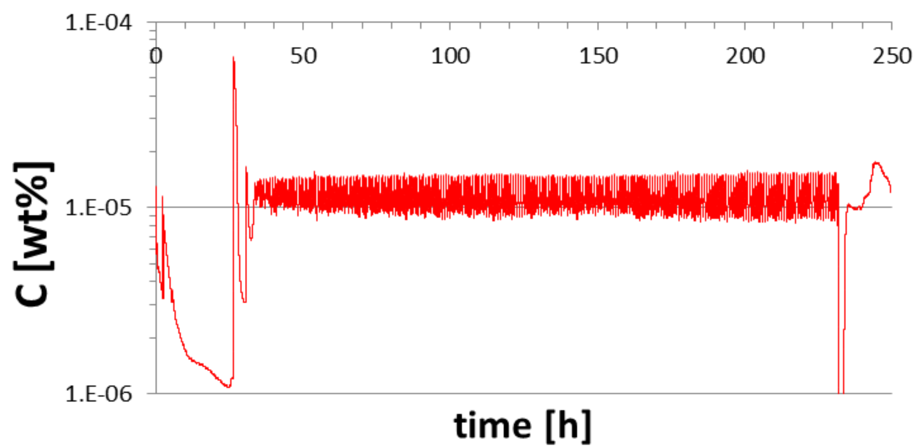
CORROSION TESTING OF CANDIDATE MATERIALS in static envrionment

Static corrosion testing

Example UCB



LBE corrosion automatic control 700°C 250h

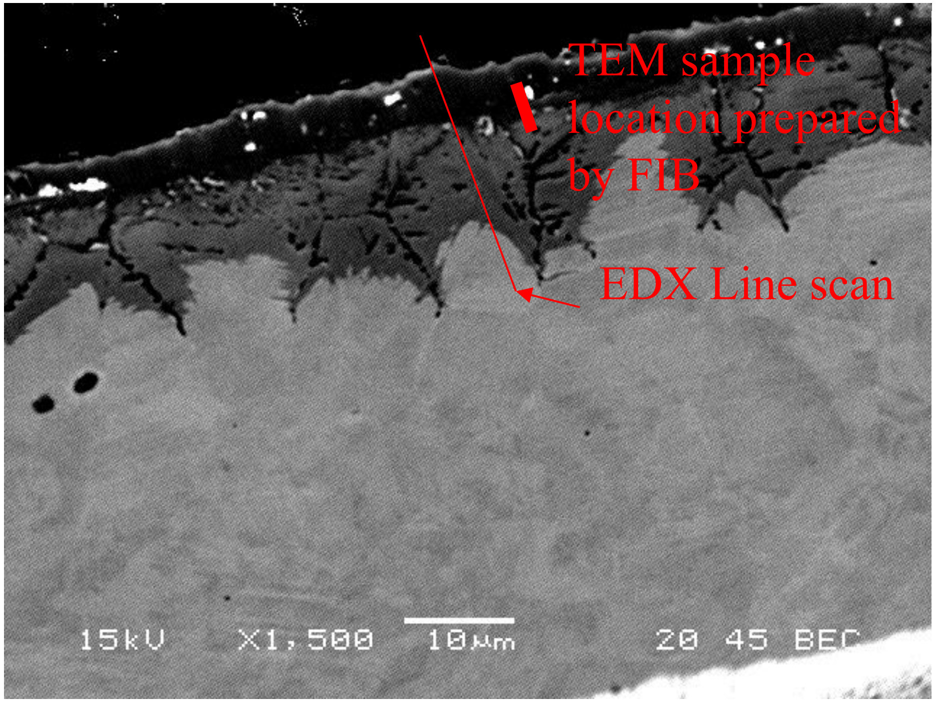


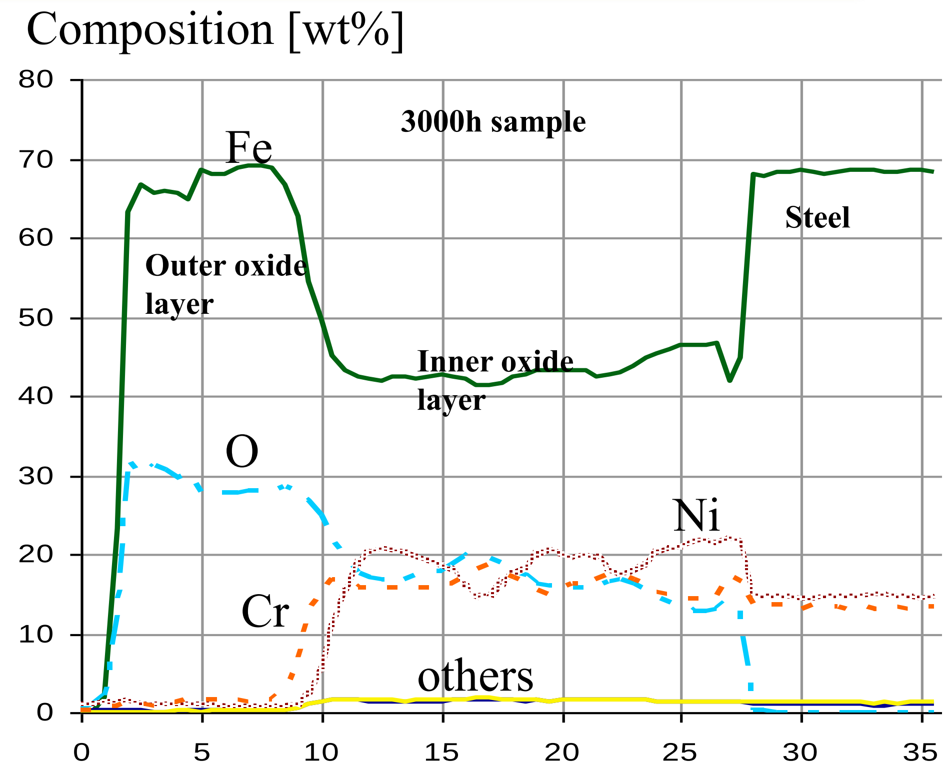
Flowing corrosion testing

Example LANL

DELTA Loop

PREVIOUS EXPERIENCE WITH AUSTENTITCS STAINLESS STEEL 3000h AT 550C (FLOWING) IN LBE (SEM)

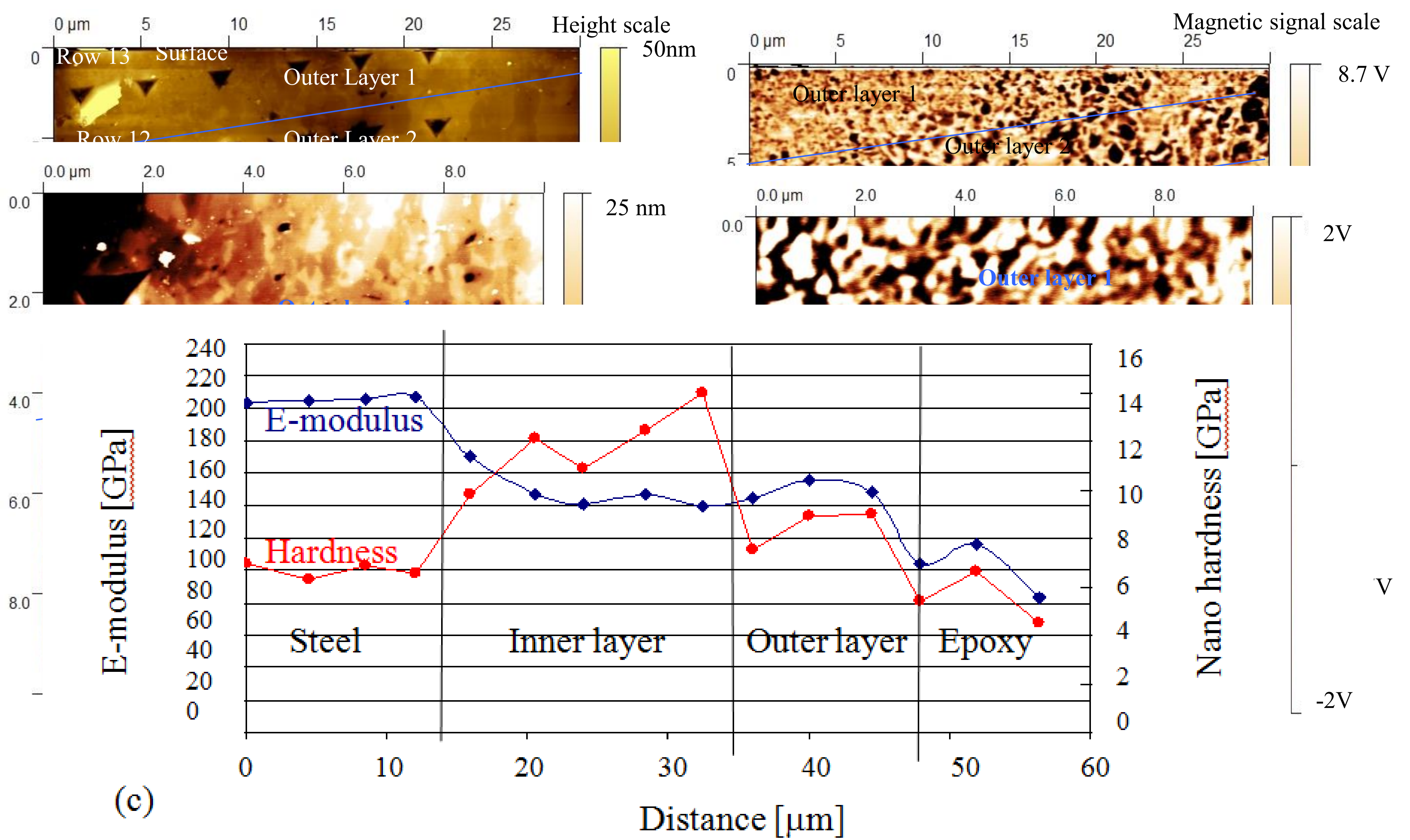




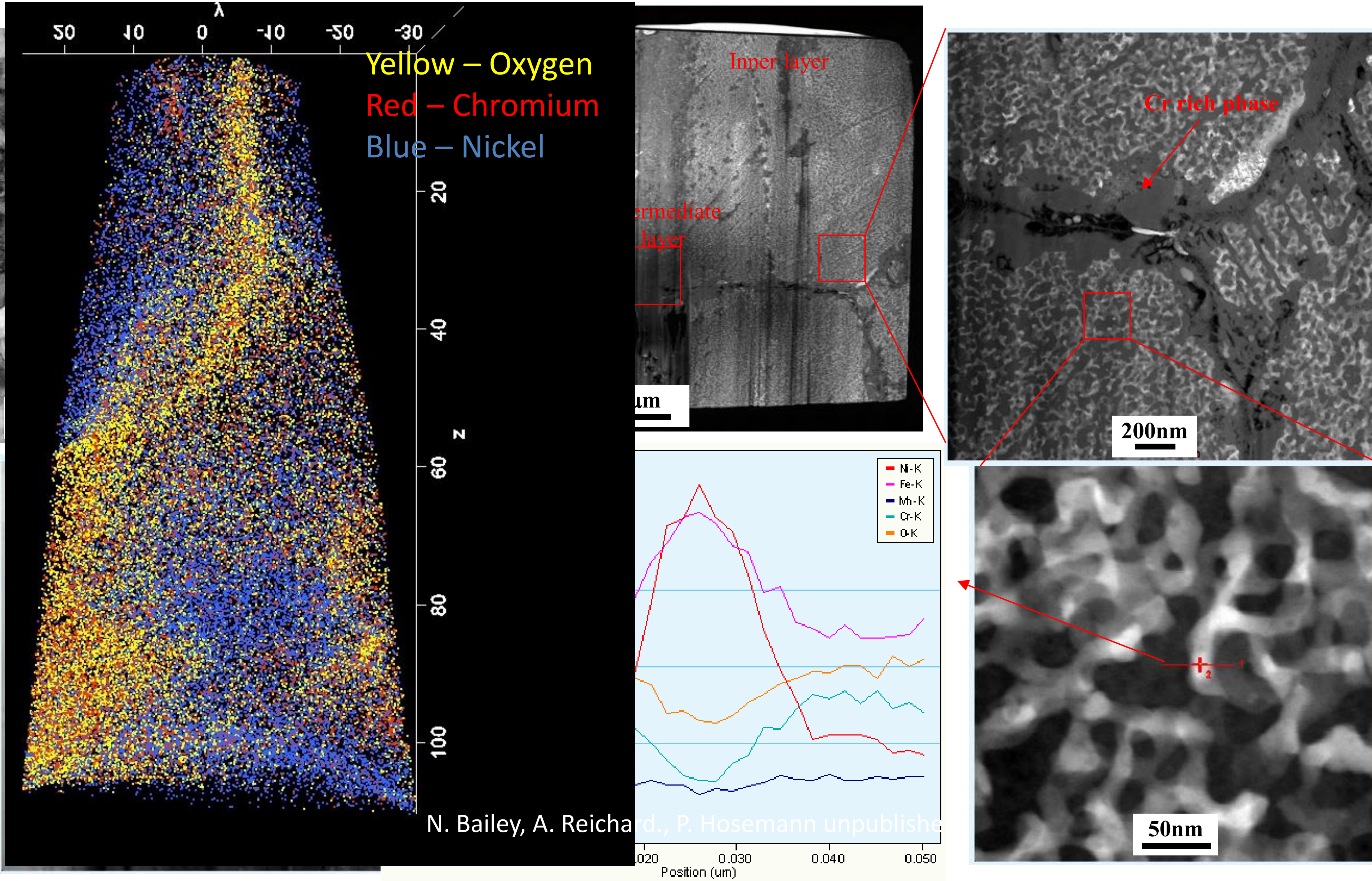
Composition: Cr 13.5-14.5 %, Ni:14.5-15.5% , Mo 2%, Mn 1.65-2.35%, Si:0.5 -0.75% , C 0.035 - 0.05%

P. Hosemann, R Dickerson, P Dickerson, N Li, SA Maloy, Transmission Electron Microscopy (TEM) on Oxide Layers formed on D9 stainless steel in Lead Bismuth Eutectic (LBE), Corr Scie. 66, (2013), 196–202

AFM MFM MEASUREMENTS ON D9 3000h, 550C, 10^{-6}wt% O_2



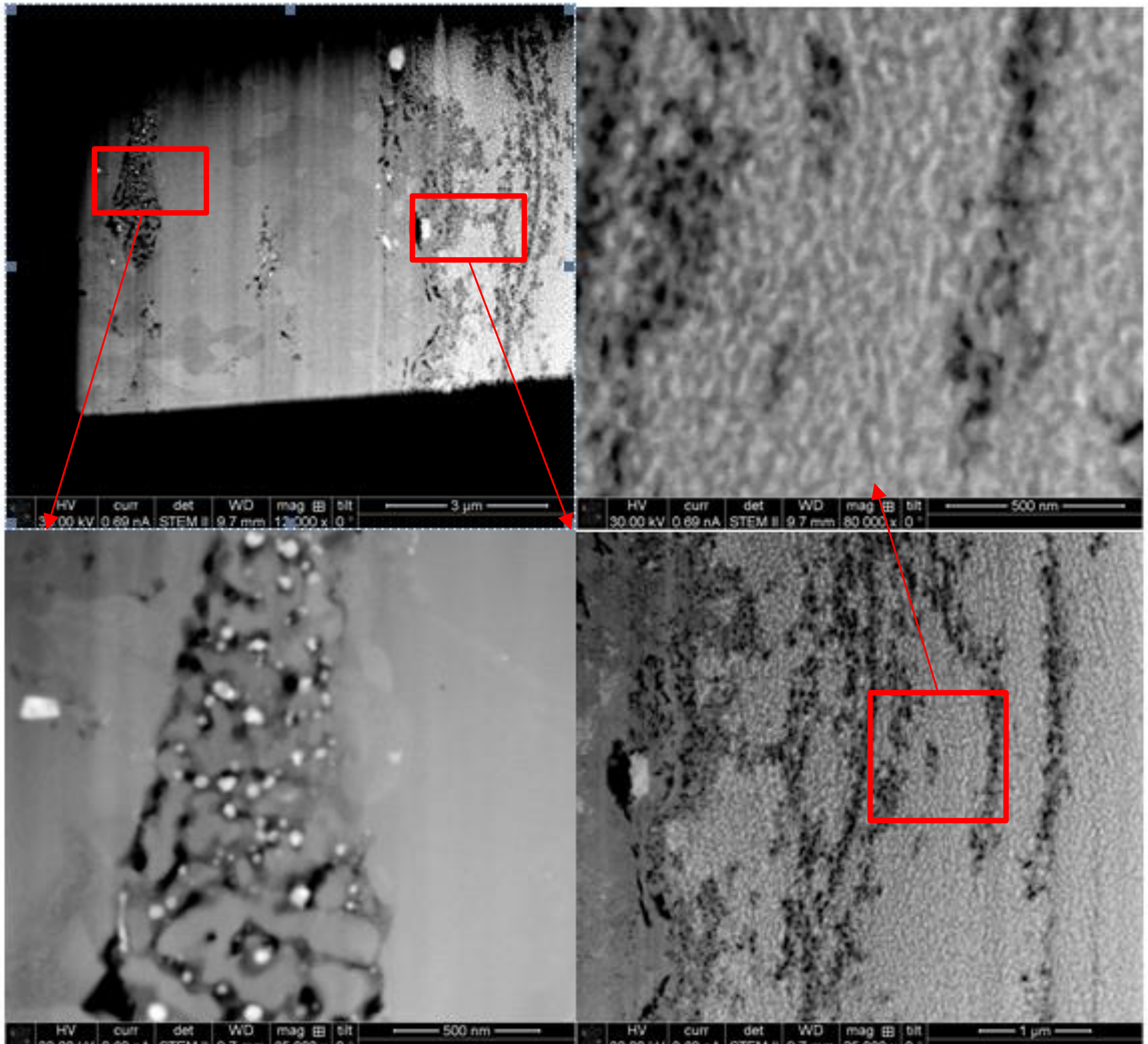
S-TEM & APT ON D9 OXIDE LAYERS



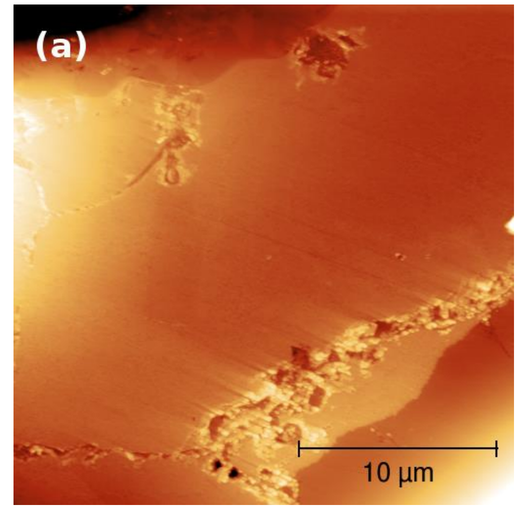
P. Hosemann et al. Corr Science 66, (2013), 196–202

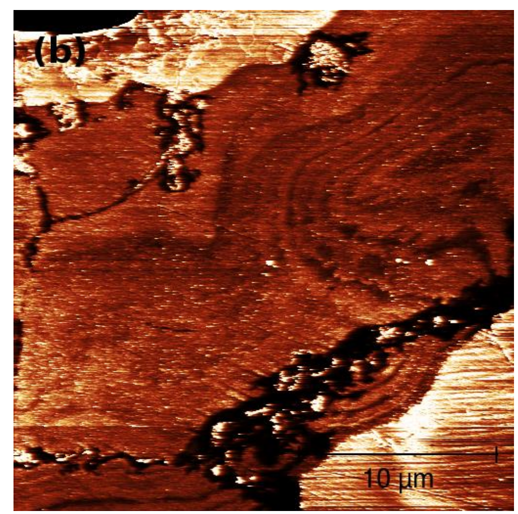
SIMILAR STRUCTURES ON OTHER AUSTENITIC STEELS
316l (3000h, 550C, 10-6wt% IPPE LOOP

STEM



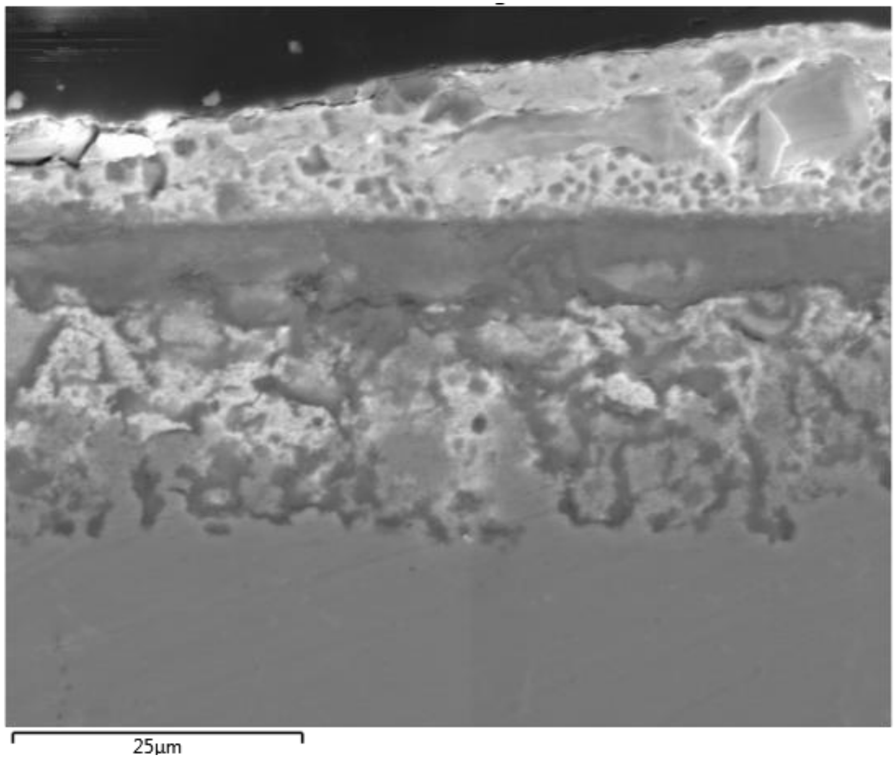
AFM

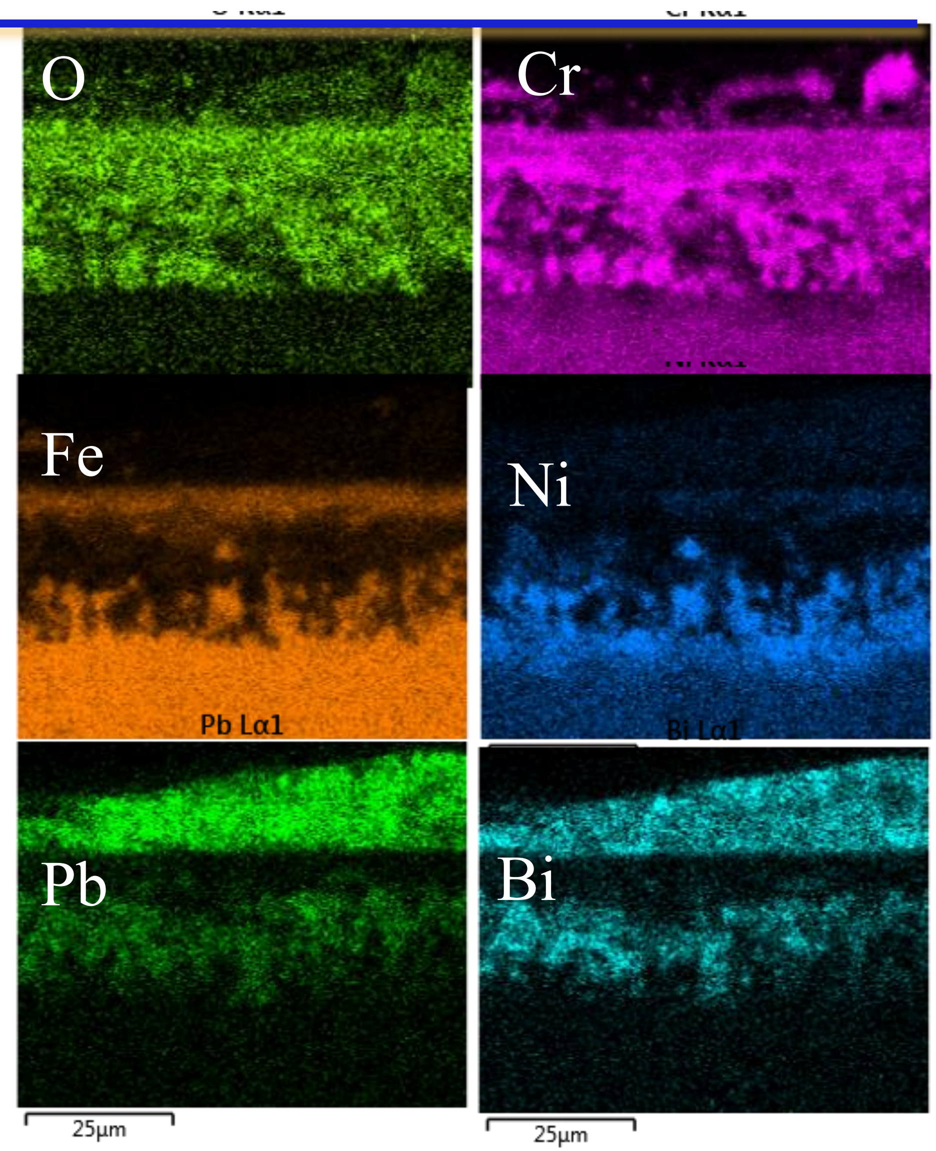




C-AFM

*MATERIALS TESTING AT **700° C** FOR 300h at 10^{-5}wt% OXYGEN (STATIC)*
316l

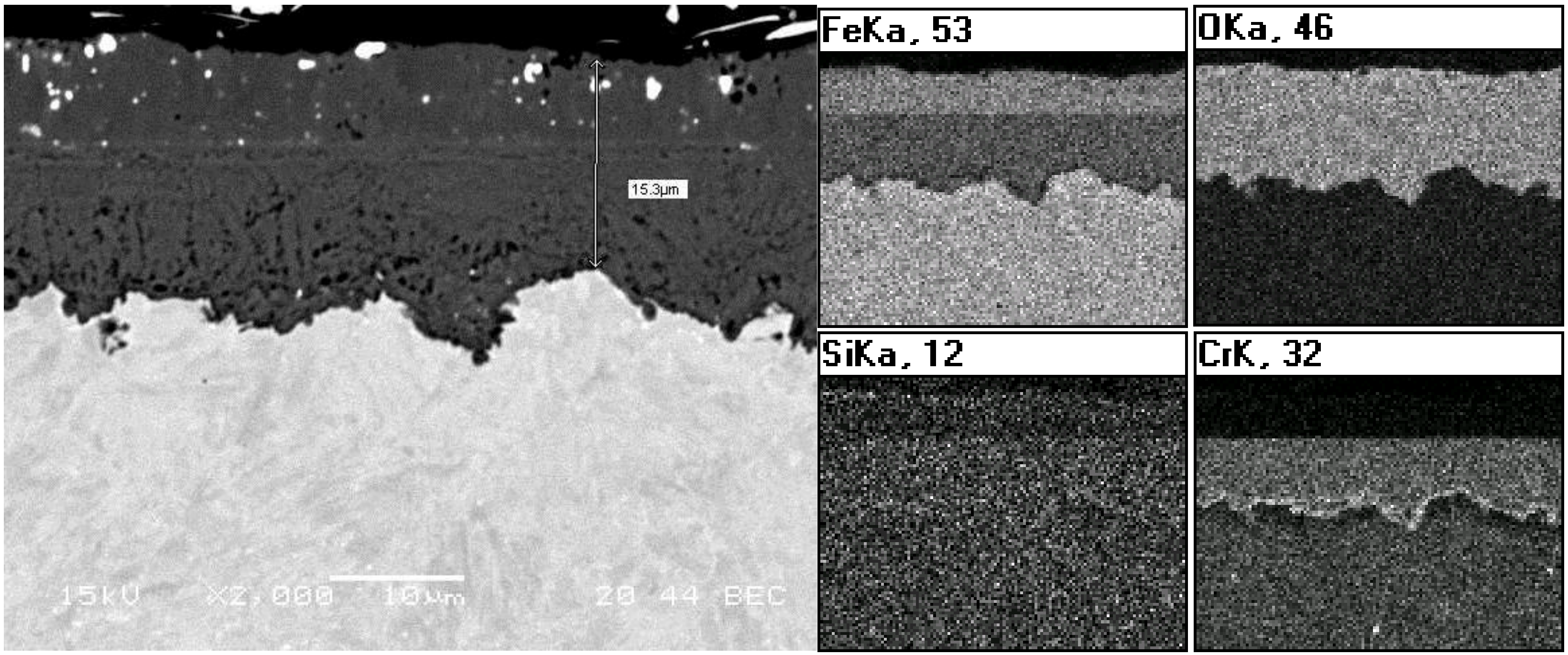




LBE penetration follows the oxide penetration.
Fast diffusion at high temperature.
→rapid progress of LM penetration

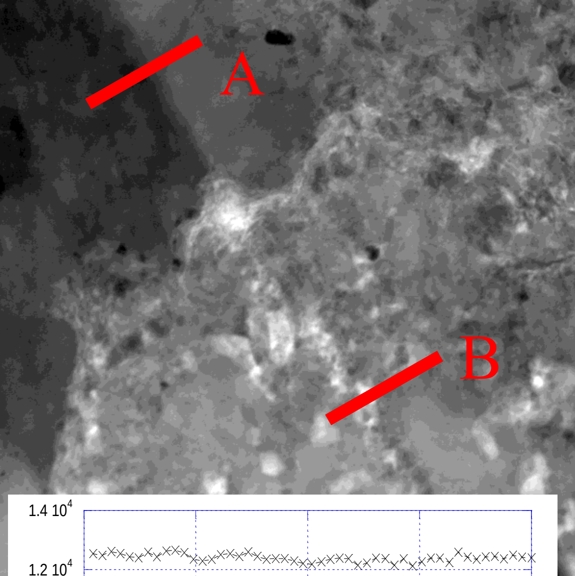
SEM/EDX ON FERRITIC STEELS

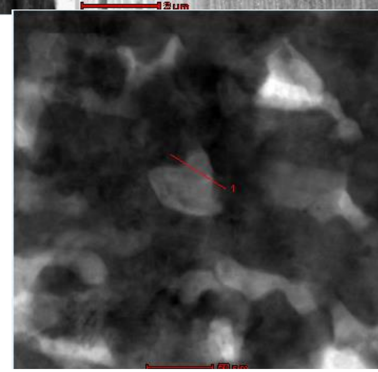
HT-9 (0.1C, 8.3Cr, 0.43Si, 0.95Mo) 3000h 550C, 10^{-6}wt% (IPPE LOOP)

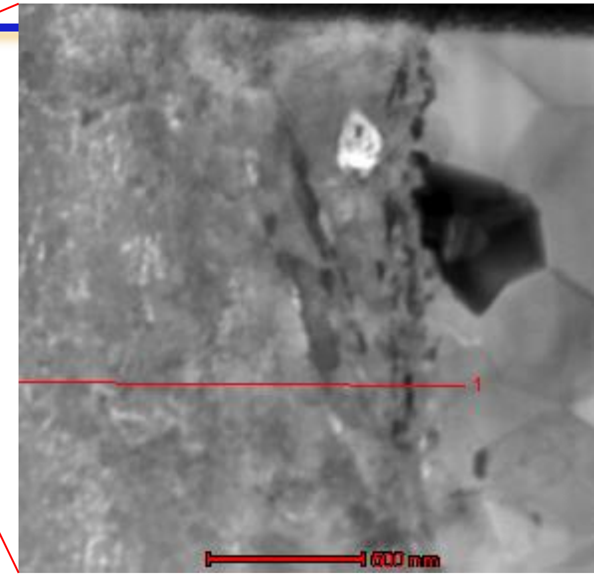


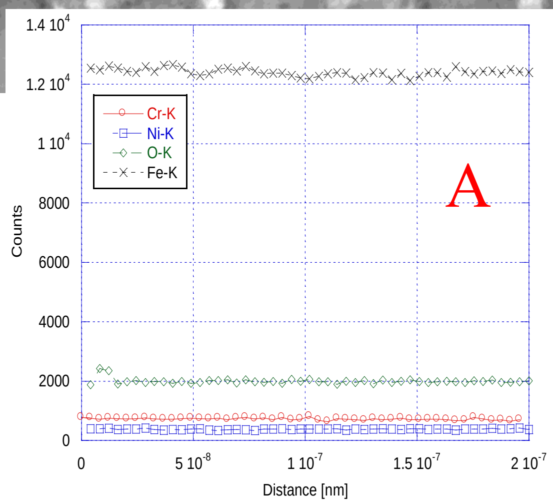
Back scattered SEM image (a) and EDX mapping of the same location on HT-9 exposed to 550C LBE for 3000h.

TEM ON OXIDE LAYERS FORMED ON HT-9

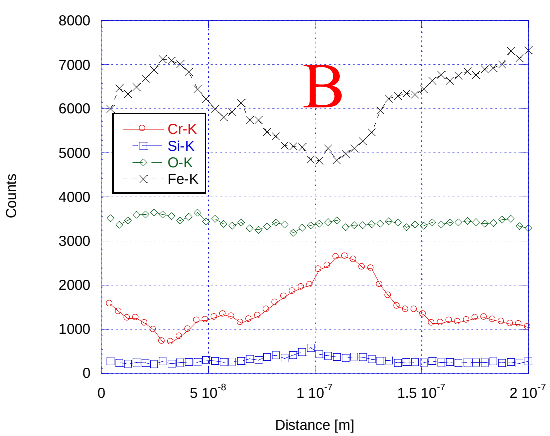




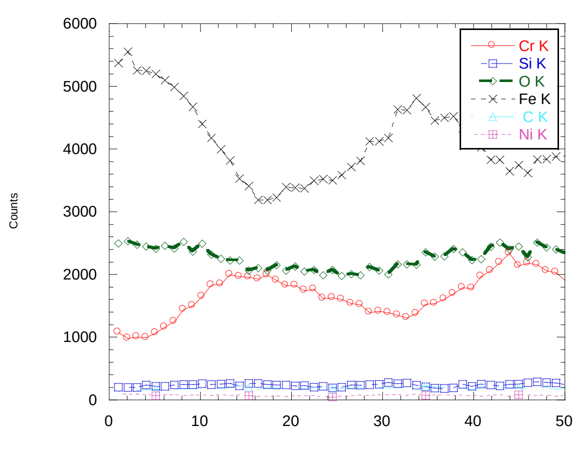




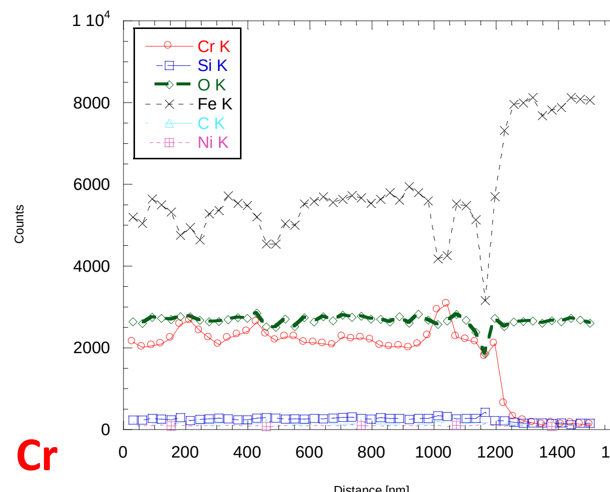
Cr
Fe
Si
O



Cr
Fe
Si
O

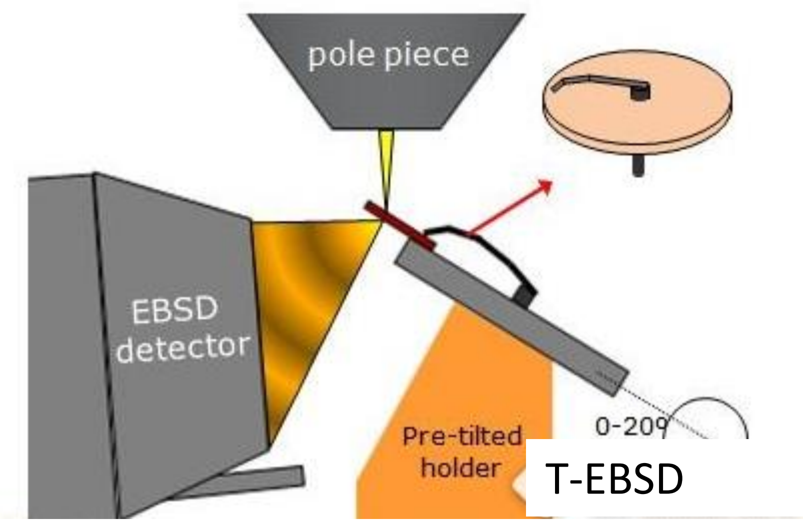


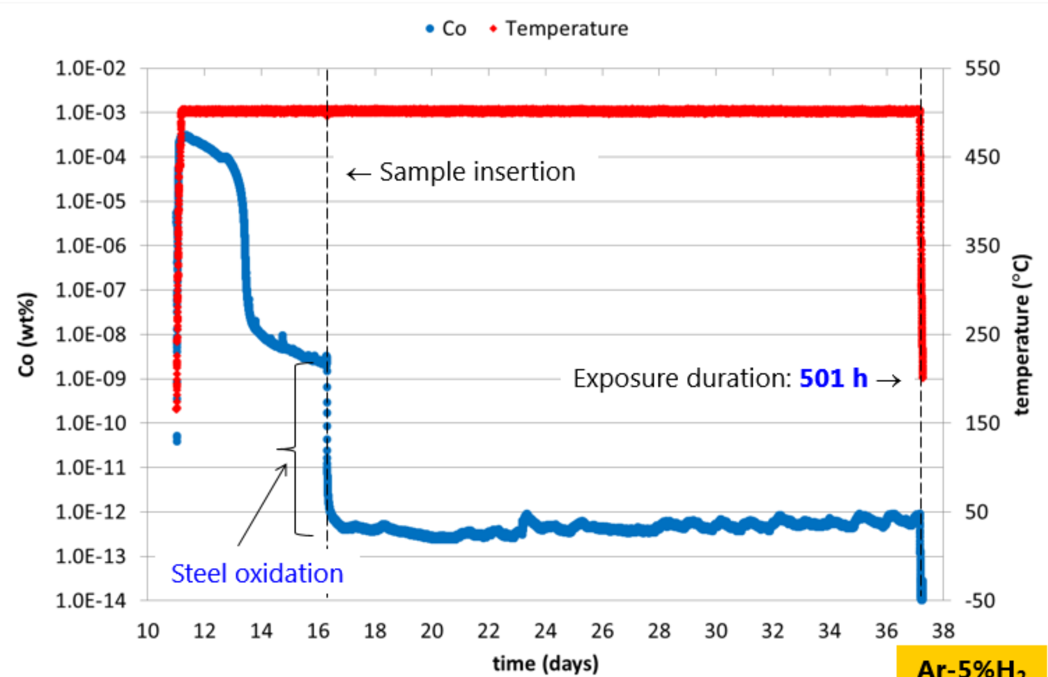
Cr
Fe
Si
O



Cr
Fe
Si
O

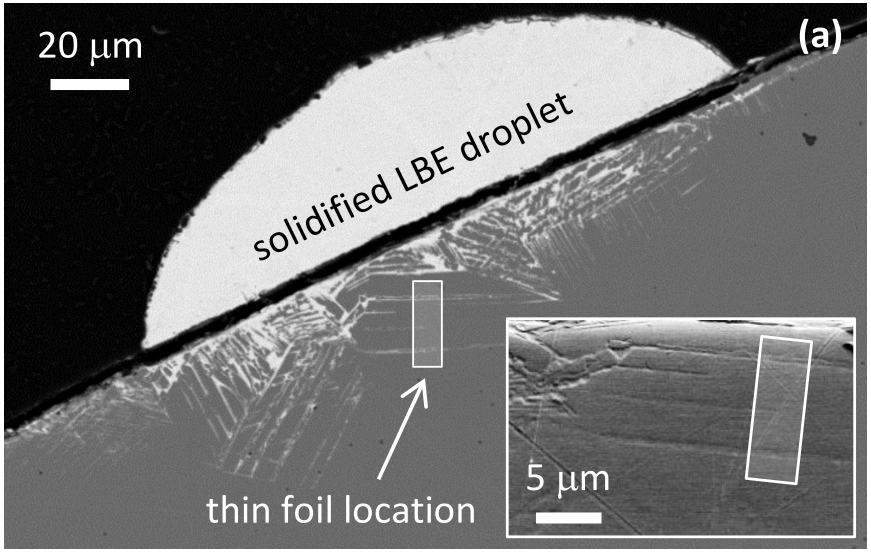
Characterization of oxide layers formed under oxygen starvation

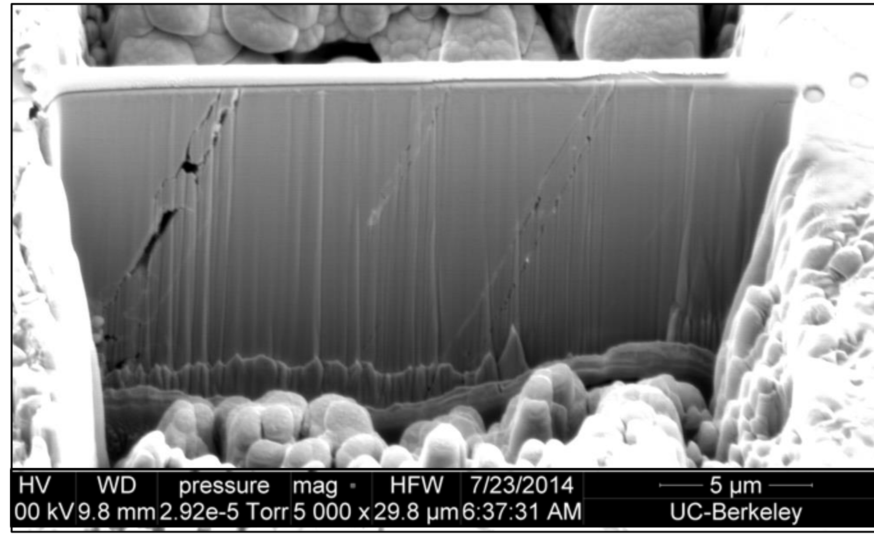


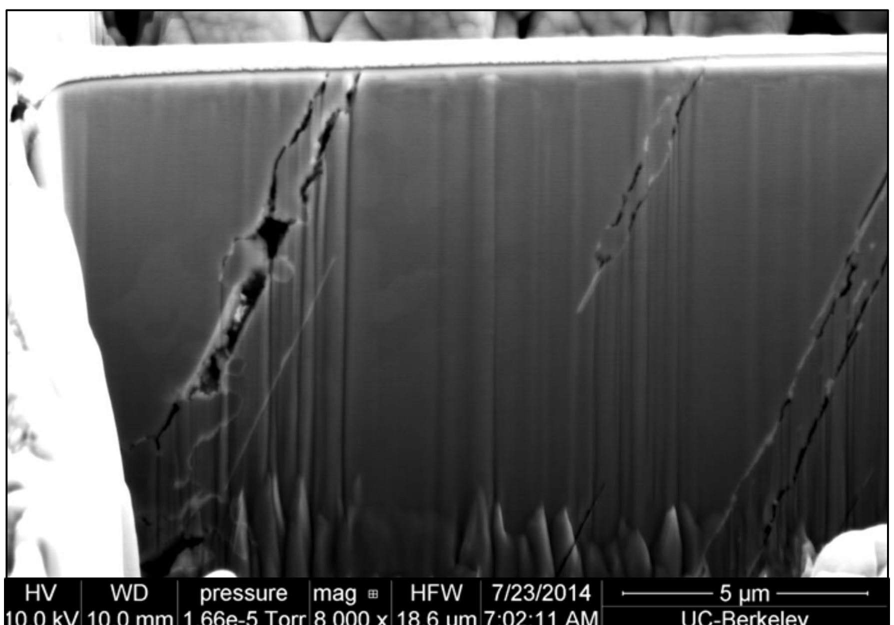


Ar-5%H_2

FIB PROCESSING ON LBE PENETRATED SAMPE; SCK SAMPLE



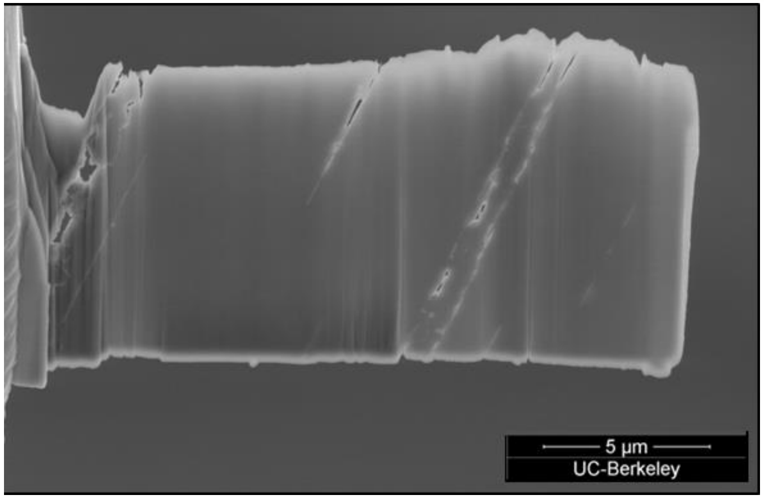


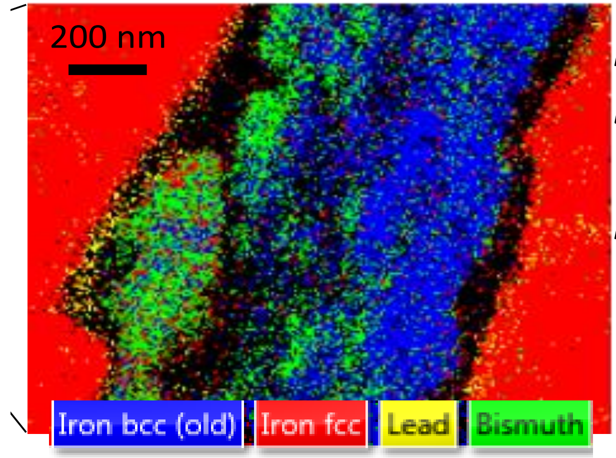


Standard FIB based lift out and slice and dice can be deployed in order to obtain the best location for a TEM sample.

316l, 450C, 1000h <<10^{-8}wt%

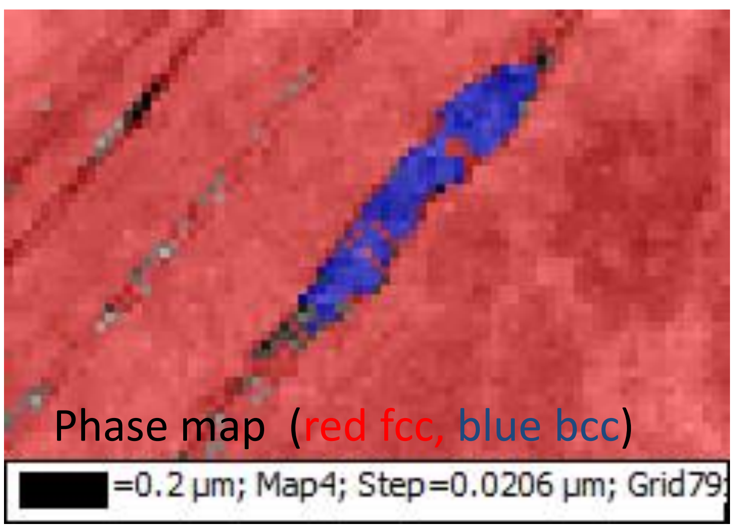
450C 1000h IN LOW OXYGEN LBE 316l SS
T-EBSD; SCK SAMPLE

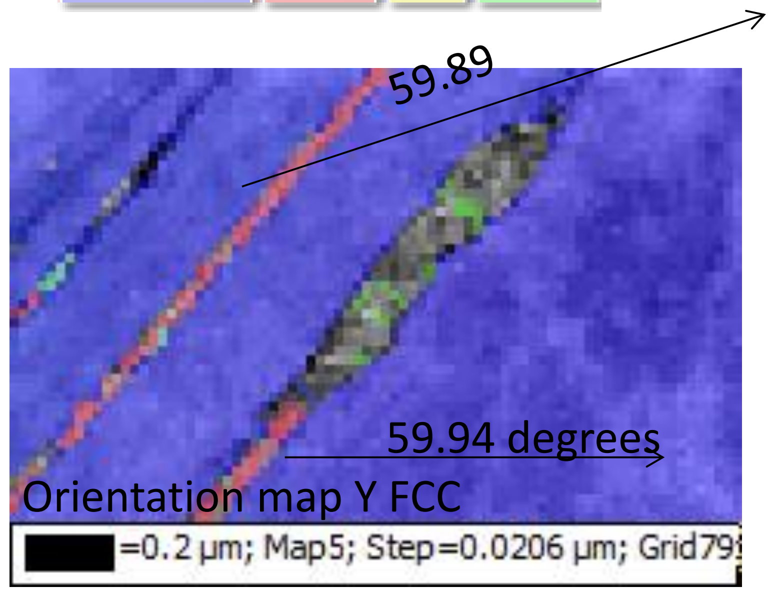


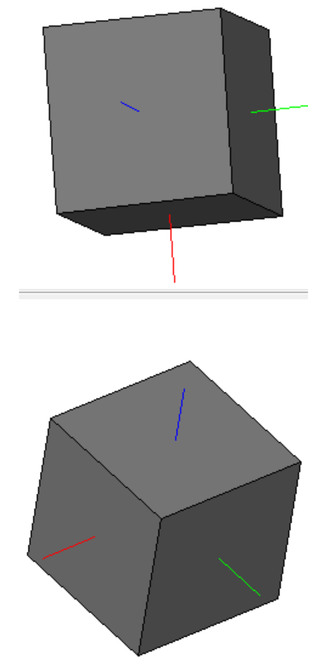


In collaboration with K. Lambrinou SCK-CEN

P. Hosemann, Submitted.







Phase transcormation fcc→bcc and
LM expansion upon freezing leads to stresses and crack formation

PUSHING THE LIMIT FOR CSP SYSTEMS WITH TEMPERATURE

High temperature;
>700C
High Flow velocity,

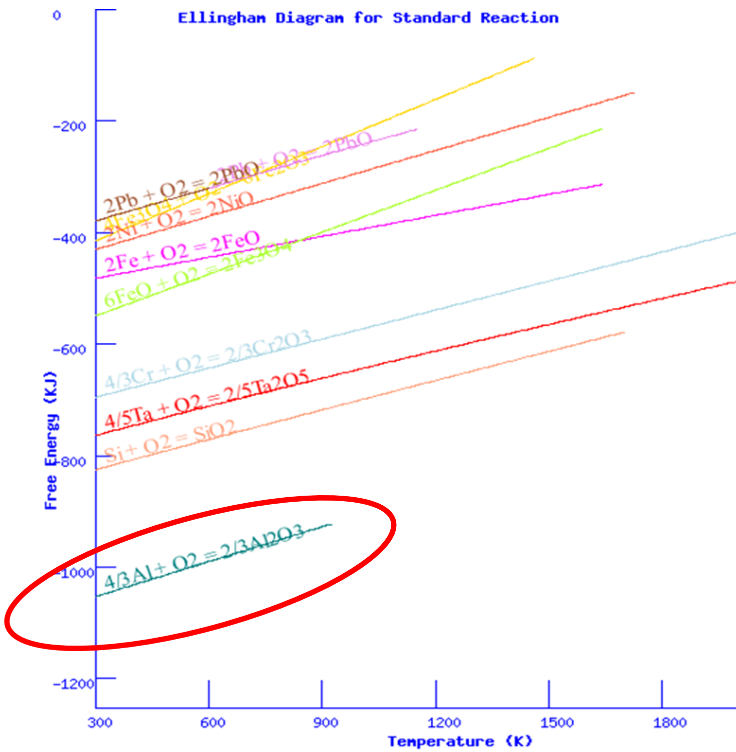
- High temperature corrosion even more of an issue in LM
- High temperature oxidation on the air side
- High temperature creep/strength issues
- Liquid metal creep issues?

→ **New structural materials selection is needed**

Best passivation film formation on common steels is Al containing steels Fe-Cr-Al alloys

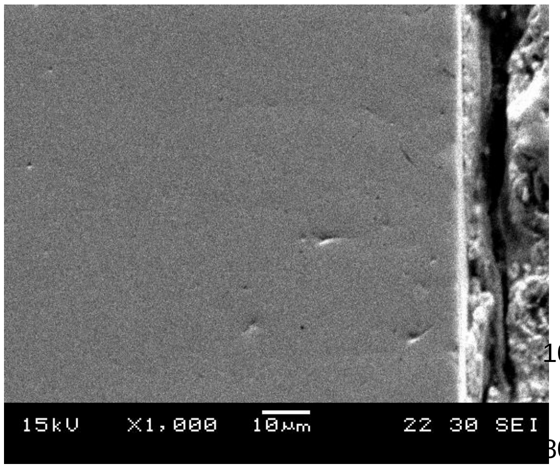
MA956, PM2000 →ODS alloys with 4.5-5.5 wt%Al

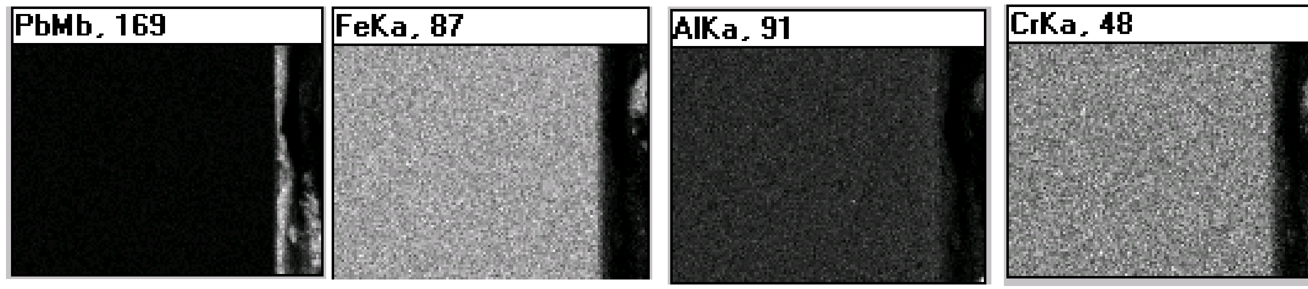
Kanthal steel series with 3-6wt%Al.



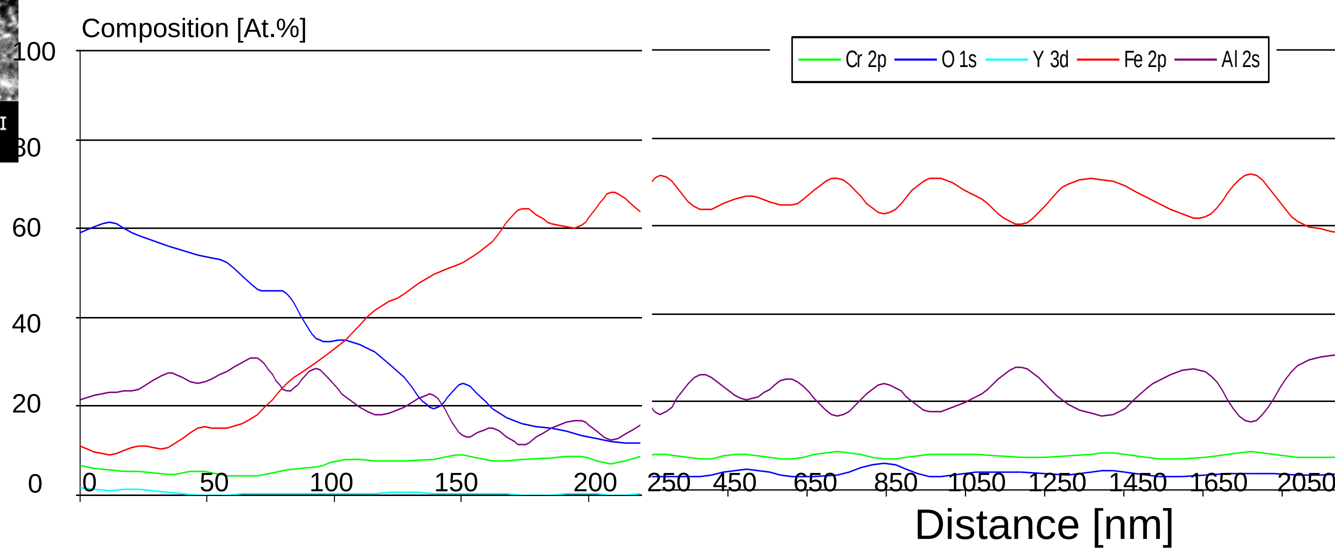
EXPERIMENTS ON PM2000 IN FLOWING LBE (600h, 535C°)

The Al-alloyed ODS steel (5.5wt%Al; 20wt%Cr; 0.5wt%Y2O3) did not show any kind of oxide layer when analyzed in cross section using SEM. Therefore a **S**putter **D**epth **P**rofiling (SDP) using **X** Ray **P**hotoelectron **S**pectroscopy (XPS) was performed to determine the composition of the very thin oxide layer on the surface of this material.



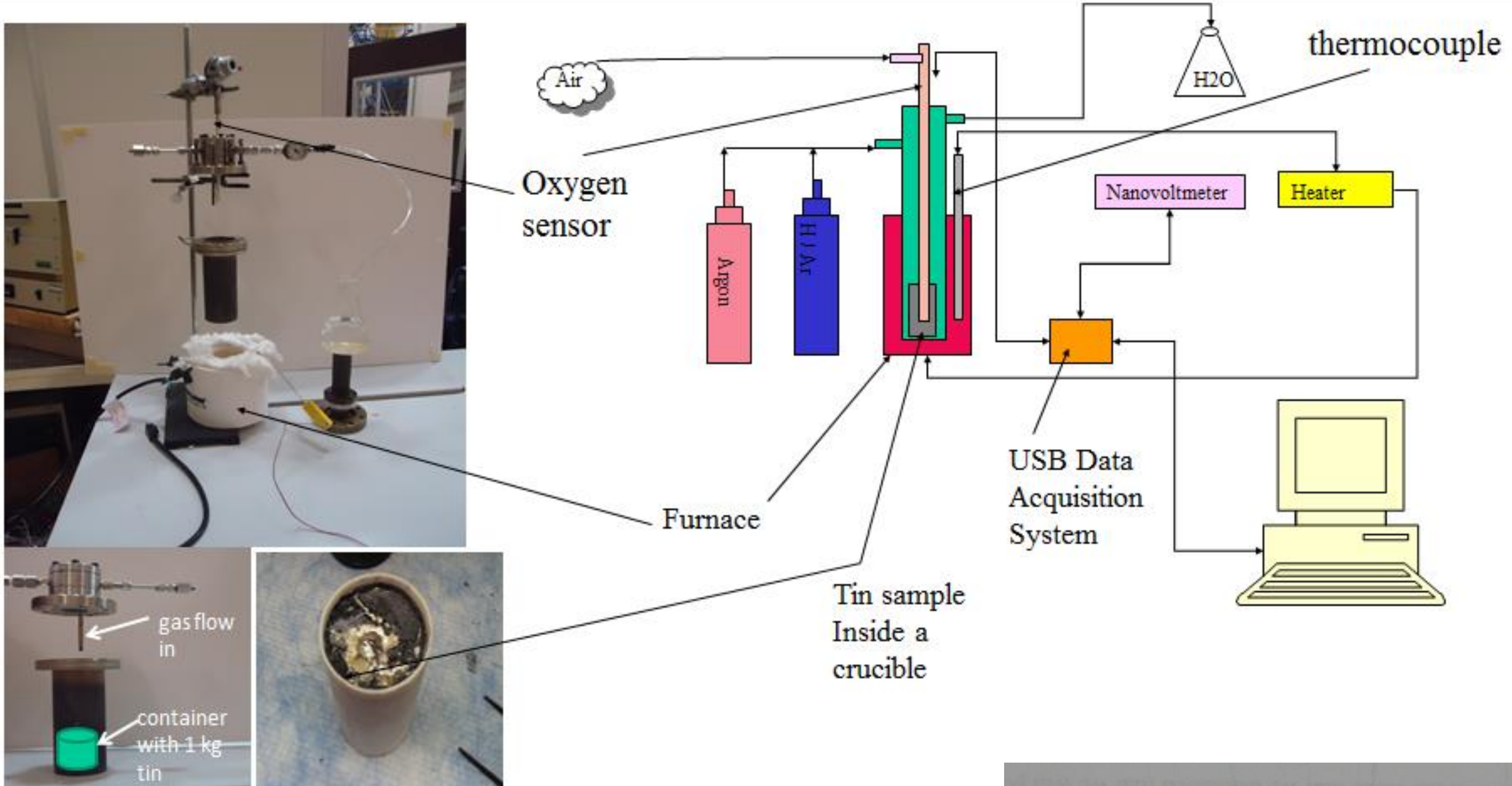


*The shallow **S**putter **D**epth **P**rofile (**SDP**) and the deep SDP using the XPS of the material PM2000 is presented. The oxide layer is Al enriched and very thin (200nm)*



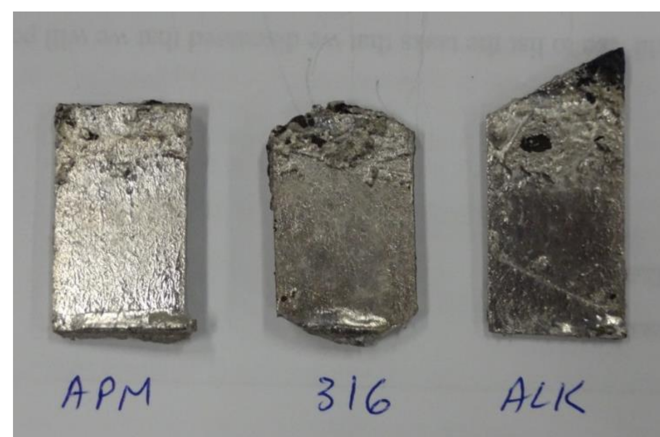
P. Hosemann, H.T. Thau, A. L. Johnson, S. A. Maloy, N. Li, "Corrosion of ODS Steels in Lead-Bismuth-Eutectic" J. Nucl. Mat. 373, 1-3 (2008) 246-253

CORROSION TESTING OF CANDIDATE MATERIALS AT HIGH TEMPERTURE

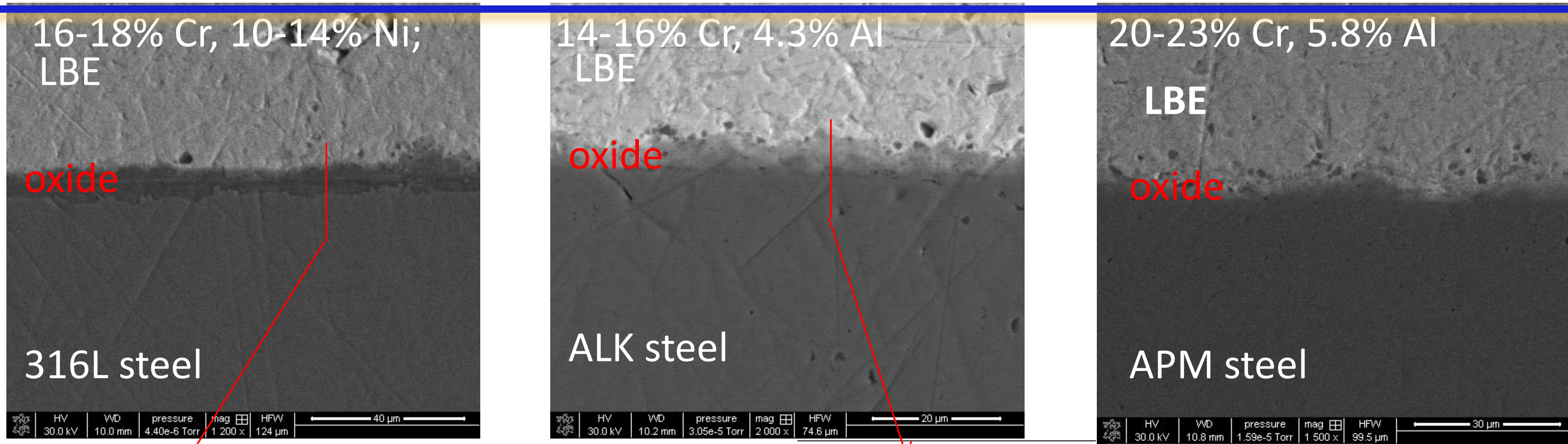


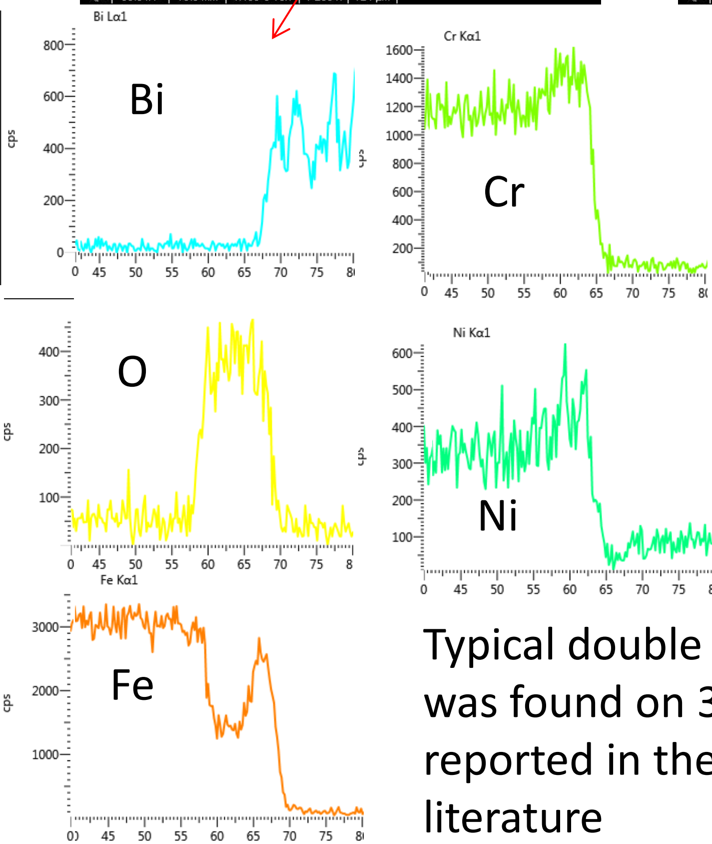
Materials selected for corrosion testing

Sample	Cr	Al	Fe	Ni
316l	16-18	-	Bal	10-14
ALK	14-16	4.3	Bal	-
APM	20-23	5.8	Bal	5.8

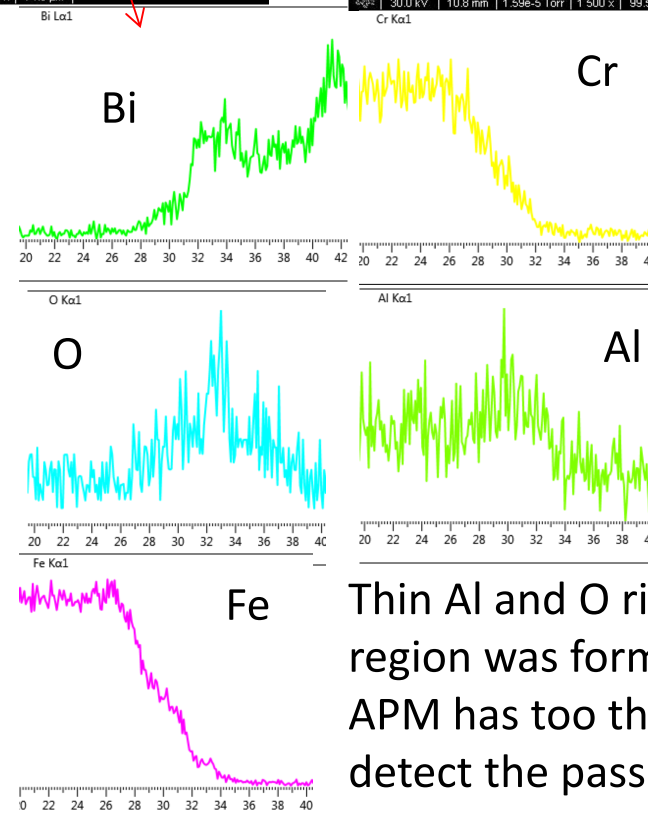


CORROSION TEST RESULTS 600°C 10^{-7} at% 500h





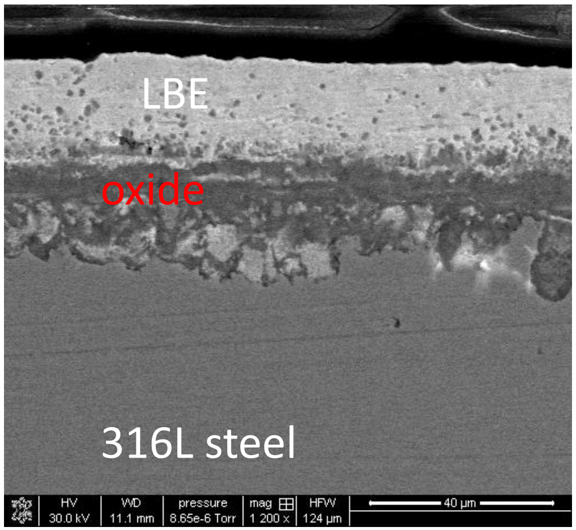
Typical double layer was found on 316l as reported in the literature

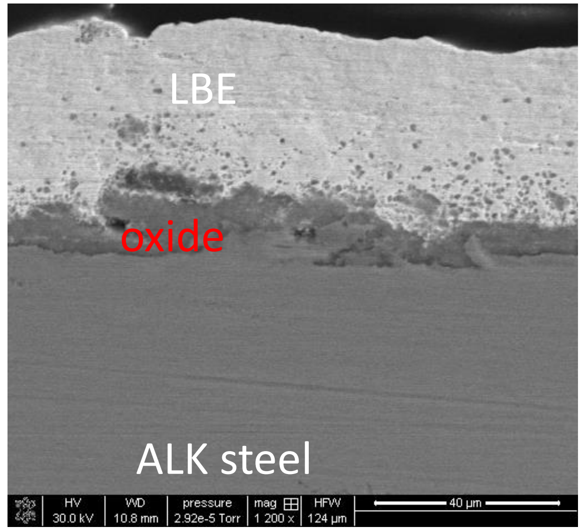


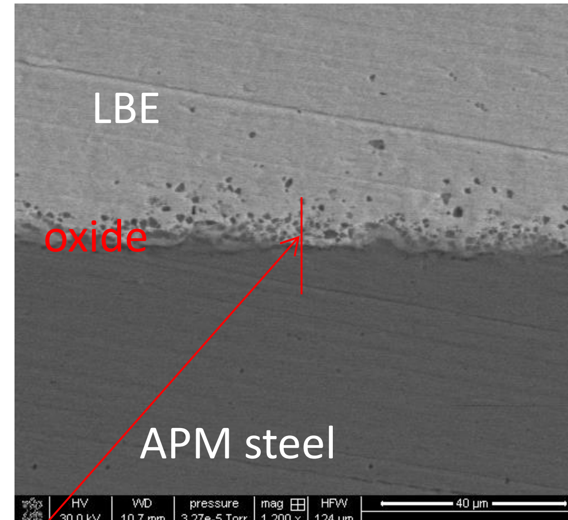
Thin Al and O rich surface near region was formed as expected. APM has too thin of a layer to detect the passivation film

CORROSION TEST RESULTS IN LBE 750°C FOR 200h 10^{-7}wt%

Test 4: 750°C for 200 h 10^{-7} wt%

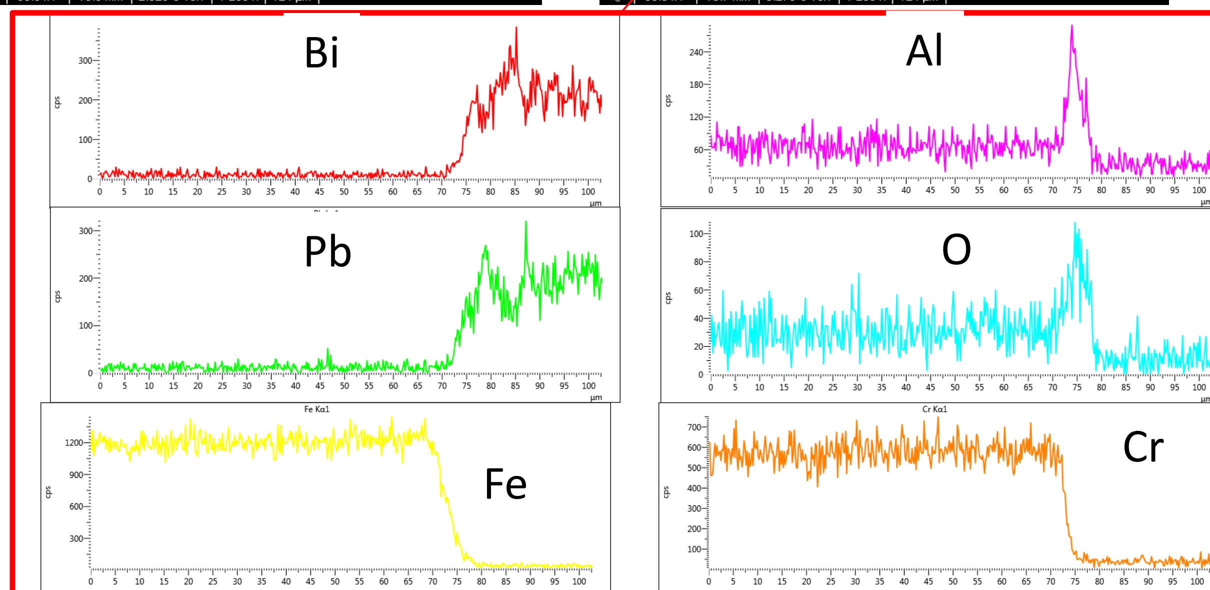






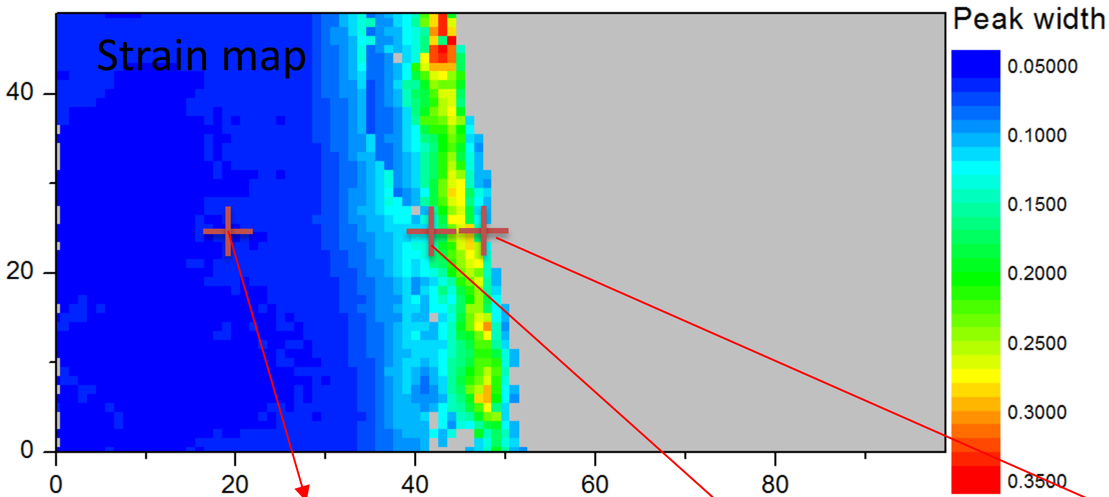
Passivation layer formed on 316l is not protective any more under this condition.

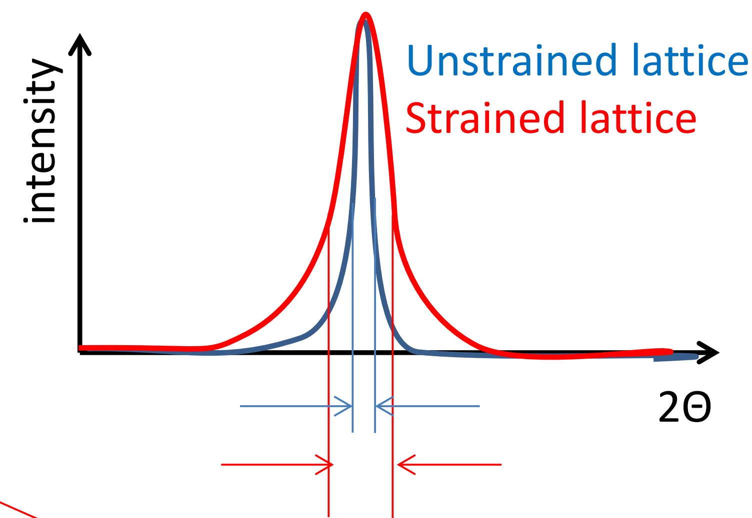
Passivation layer on Al containing steels appears to be sufficient.



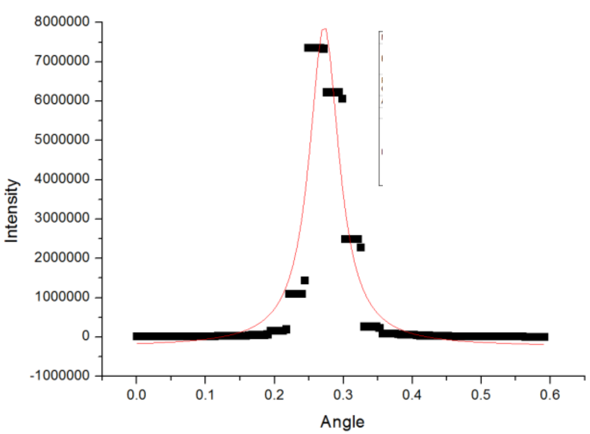
STRAIN UNDERNEATH THE OXIDE LAYER AFTER COOLING THE SAMPLE STUDIED USING LAUE MICRO DIFFRACTION

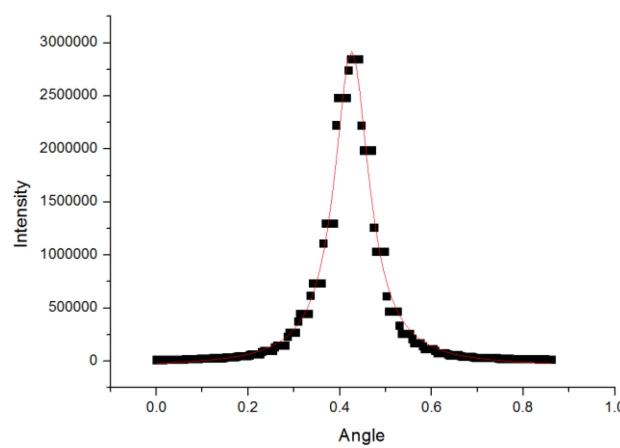
Kanthal ALK 700°C 500h

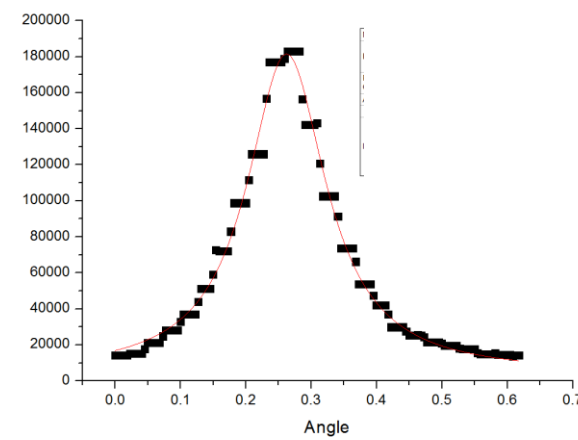




Peak shape change as a function of location







HIGH VELOCITY FLOW EXPERIMENT AT LANL (LBE)

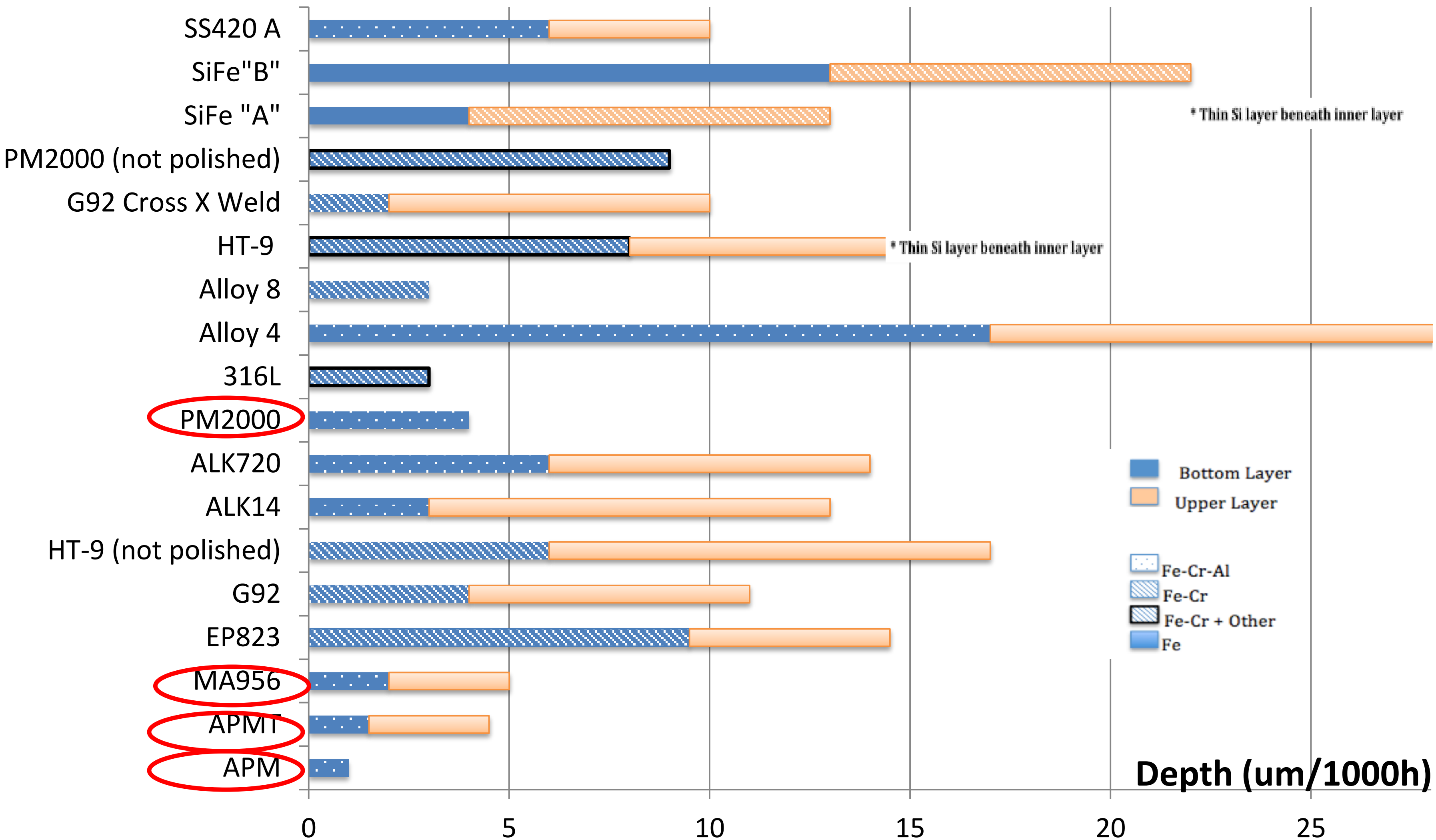
Samples	Oxide thickness
APM	1 µm
APMT	5 µm
MA956	5 µm
EP823	10 µm
G92	10 µm
HT-9 (not polished)	20 µm
ALK14	15 µm
ALK720	10 µm
PM2000	1 µm
316L	3 µm
Alloy 8	5.5 µm
HT-9	18 µm
G92 Cross X Weld	12 µm
PM2000 (not polished)	12 µm
SiFe "A"	13 µm
SiFe"B"	20 µm
SS420 A	12 µm
Alloy 4	

Flow conditions	
T [C]	488
Velocity [m/s]	3.5
Oxygen concentration [wt%]	3.2×10^{-5}

We were able to provide samples for the LANL corrosion loop

M. De Caro, S.A. Maloy, F. Rubio
Los Alamos National Laboratory

RESULTS OF HIGH VELOCITY TESTING OF VARIOUS STEELS LBE 535°C 1000h



Hi Cr and high Al alloys perform the best even at high flow velocity

Investigating the strengths of the passive layers.

A parameter of mechanical adherence

MECHANICAL STABILITY OF PASSIVE LAYERS FORMED IN LBE

Additional questions raised:

Mechanical strength of the oxide layers?

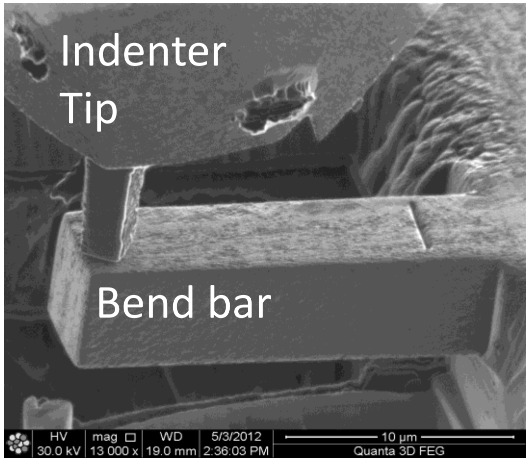
Interface strength between steel and passive layers?

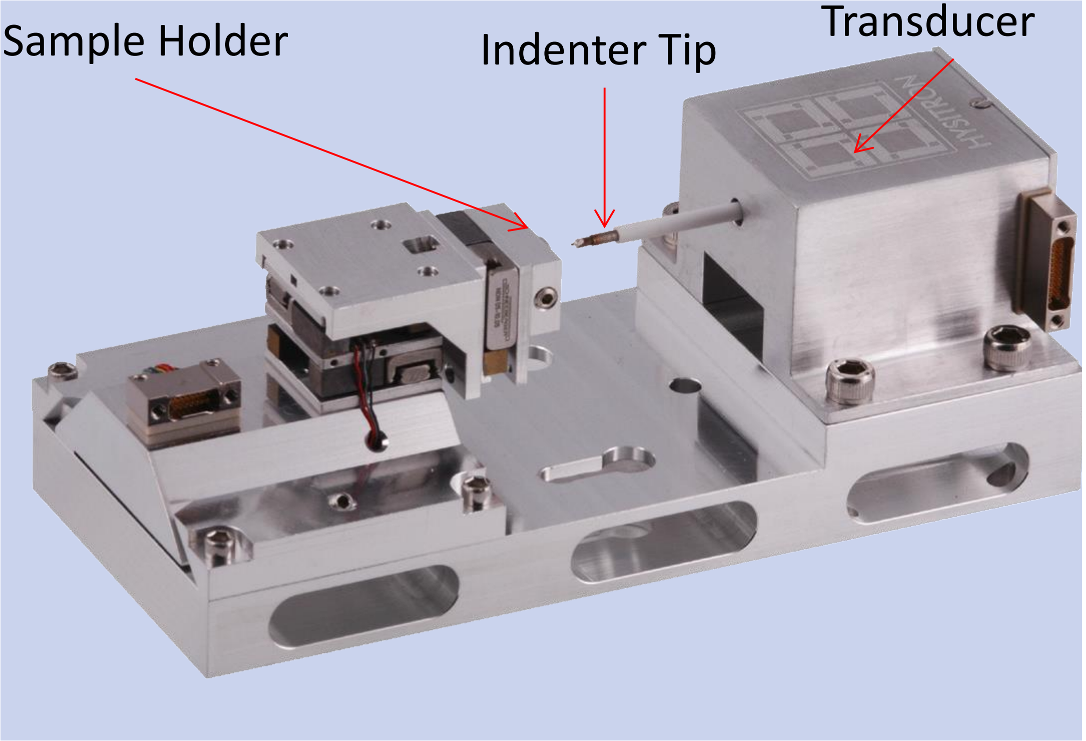
Fracture surface and fracture mode of the passive layers?

Initial experiments were designed to evaluate the questions above.

M. D. Abad et al; Oxid. Met. 2015

In-situ testing in the SEM using a Hysitron PI85 picoindenter



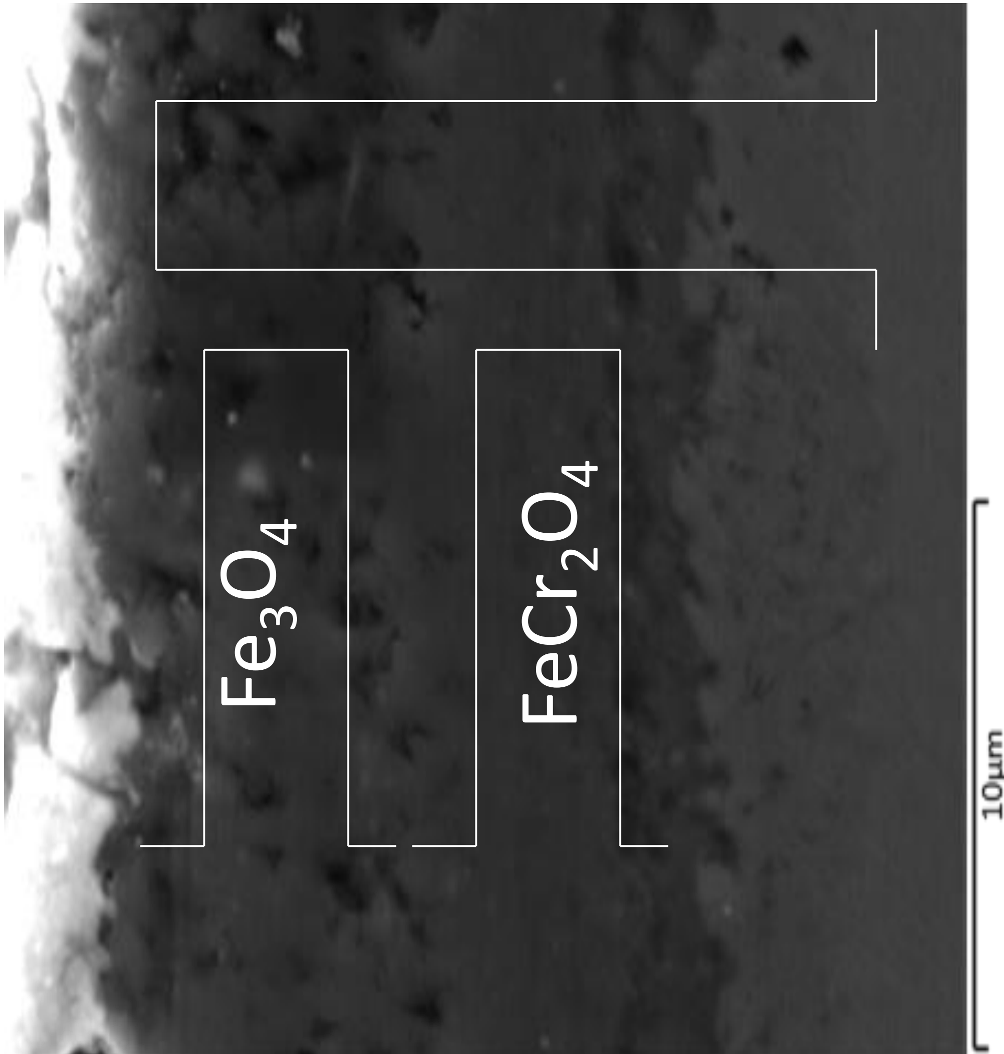


INVESTIGATING MECHANICAL STABILITY OF PASSIVE FILMS, BRITTLE FRACTURE

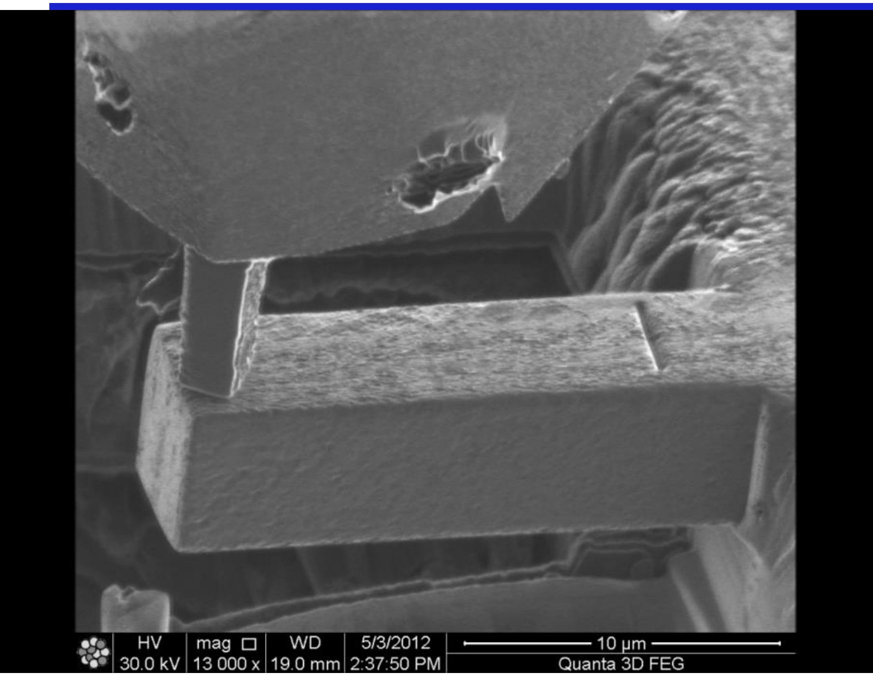
Micro Cantilevers milled at the University of California, Berkeley

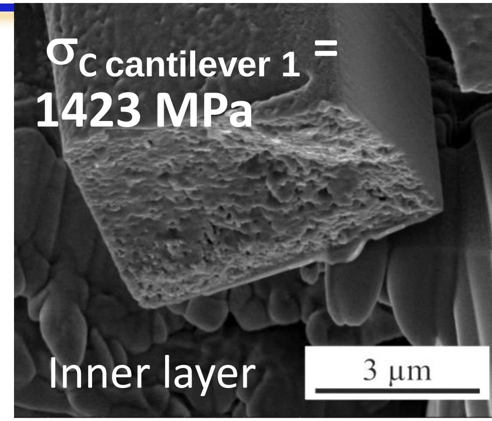
Milled using a FEI Quanta 3D FEG Focused Ion beam instrument

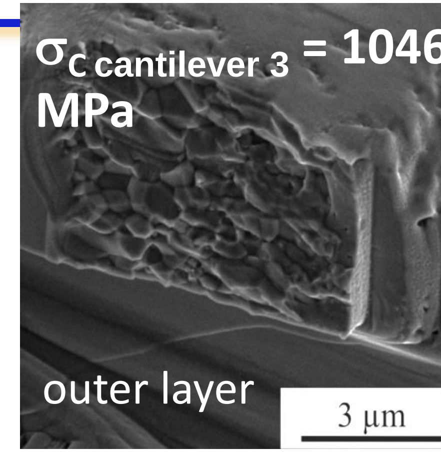
Ferritic/martensitic steel ***HCM12A*** after exposure to LBE.
Sample provided by K. Kikuchi

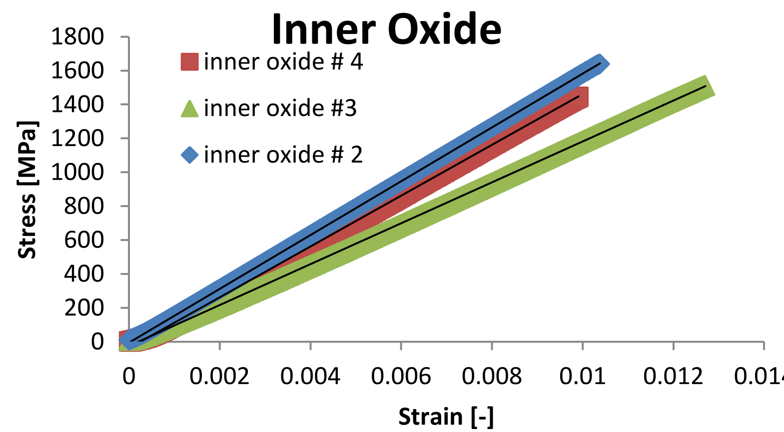


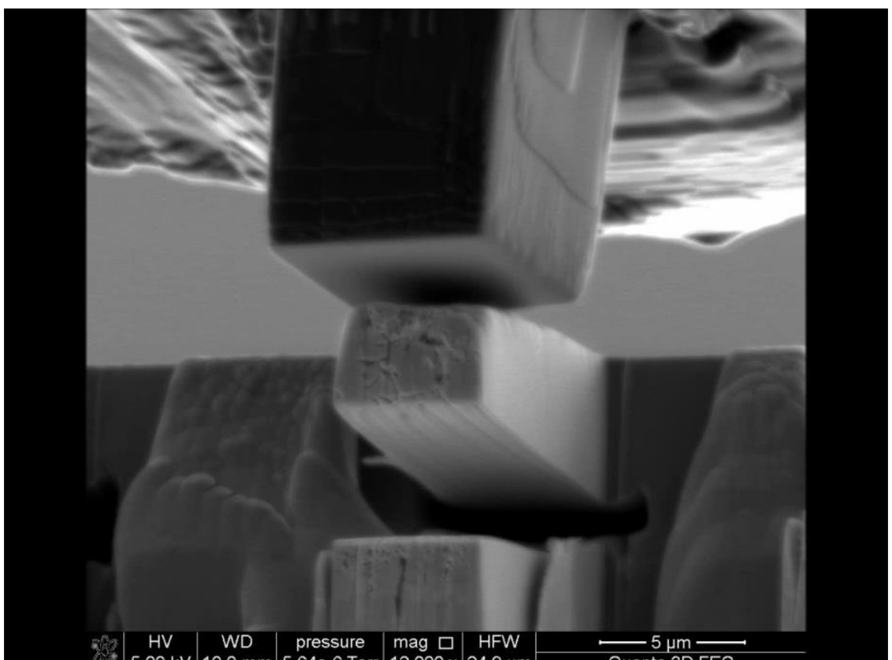
IN-SITU FRACTURE TEST

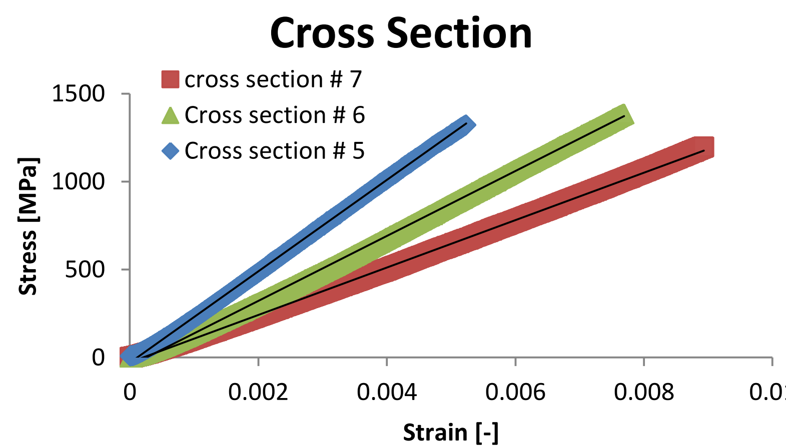




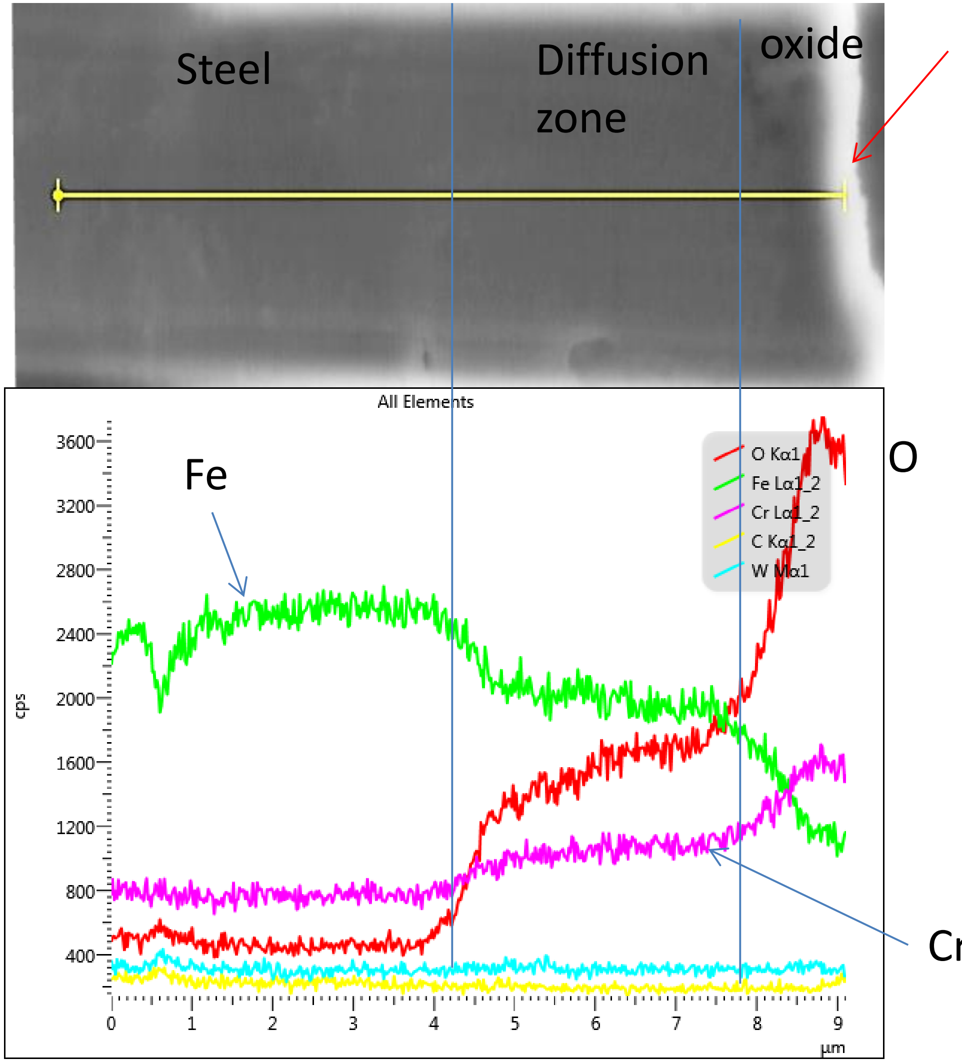








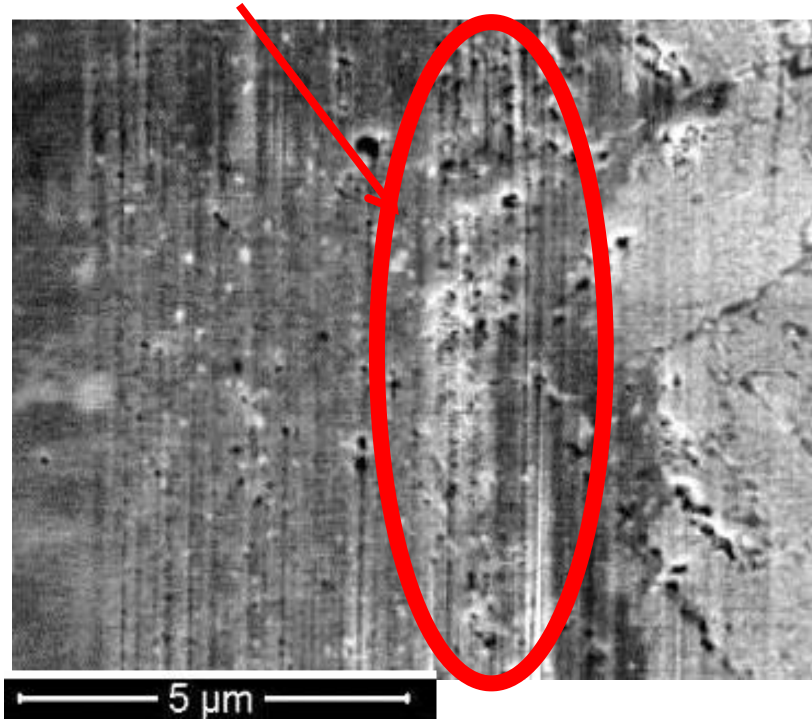
POST FRACTURE ANALYSIS



Fracture Surface

Fracture occurs in the porous area not directly at the interface!

High porosity region
Fracture region

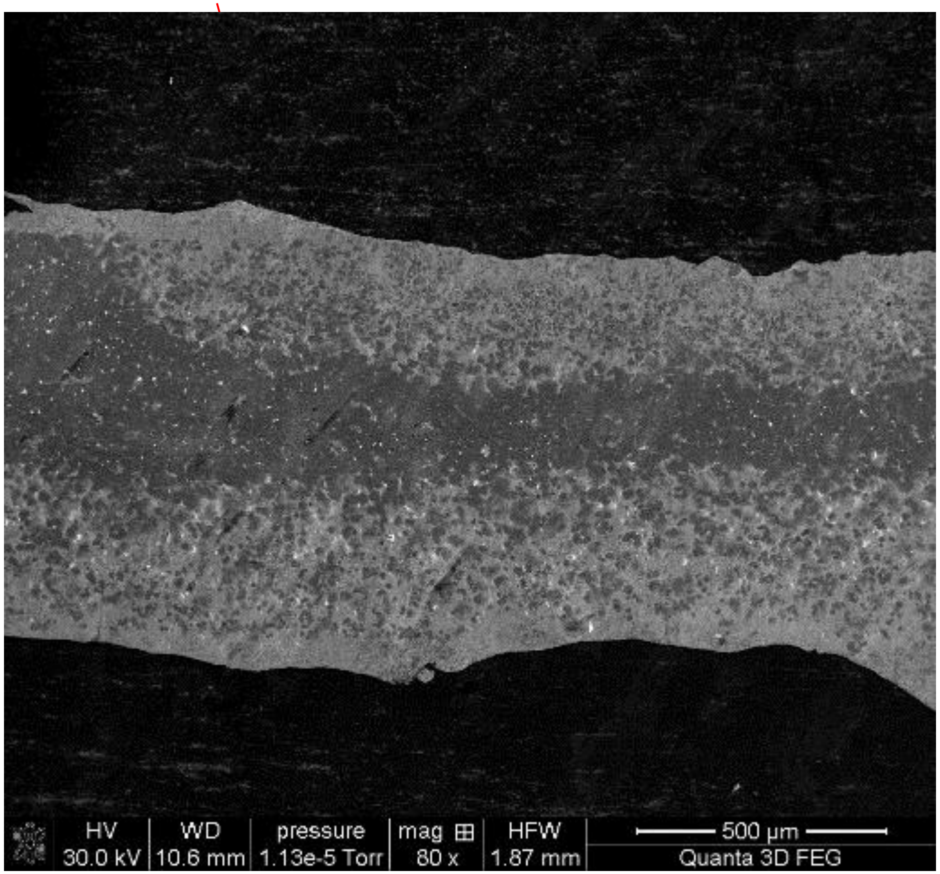


M. D. Abad et al; Oxid. Met. 2015

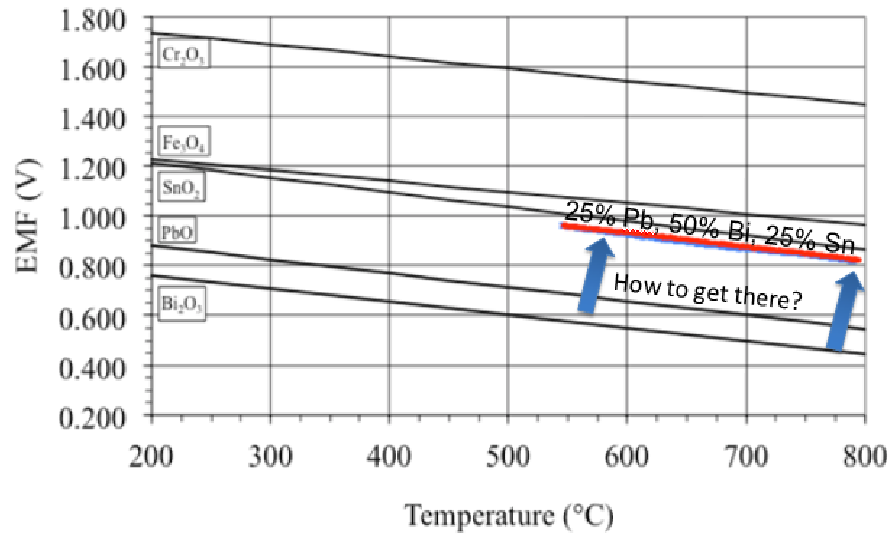
Other liquid metals may be considered for CSP

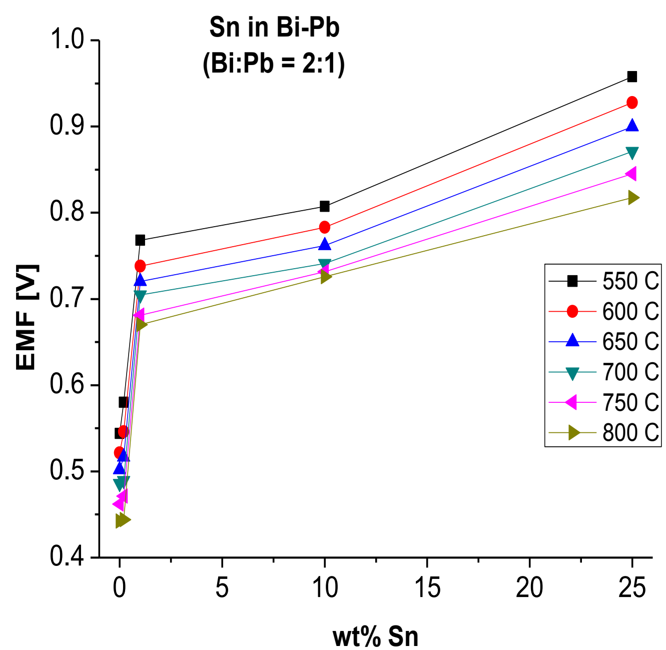
SMALL AMOUNTS OF ADDITIONAL ELEMENTS AFFECT OXYGEN POTENTALS.

APM Kanthal steel 700°C, 1060h near oxygen saturation (50Bi/25Pb/25Sn)



EMF measurements of oxygen-saturated Rose's metal

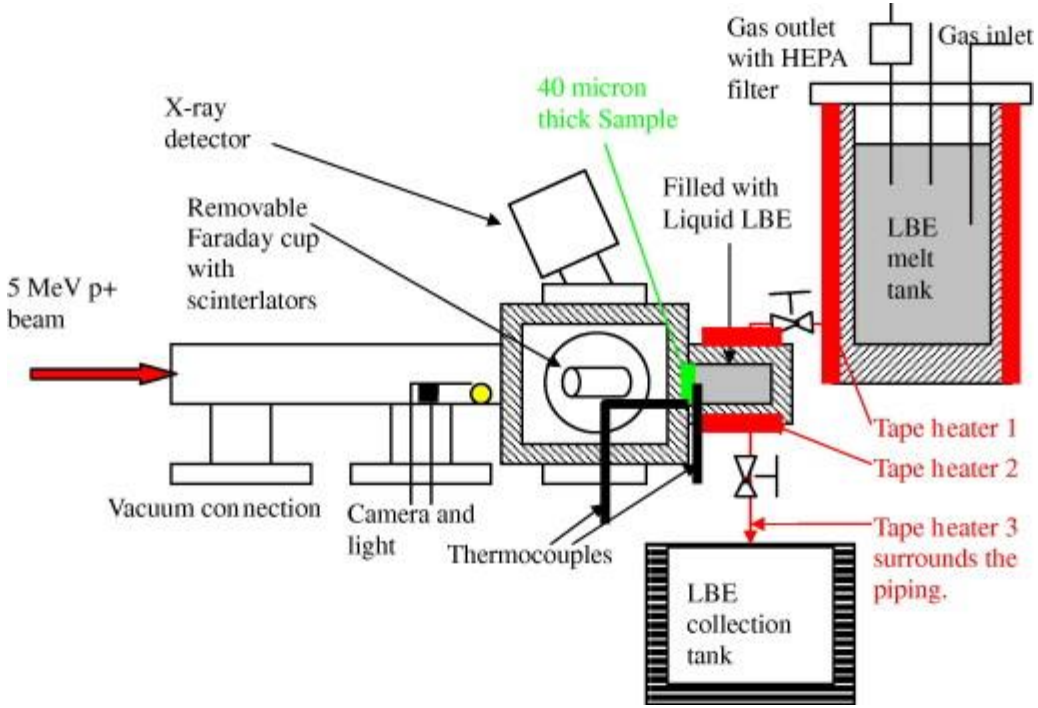




The irradiation and corrosion experiment (ICE)

THE IRRADIATION AND CORROSION EXPERIMENT (ICE) DESIGN

Hosemann et al. , J. Nucl. Mat. 376 (2008) 392.



Beam: 5 MeV protons, 0.5 µA current, 80 hour run
Target: Concaved HT-9 foil, 40 um at the center, 350 ºC
Damage level: 0.3 to 1.4 dpa
LBE chemistry control: no oxygen sensor
Corrosion rate change due to irradiation is not important/noticeable

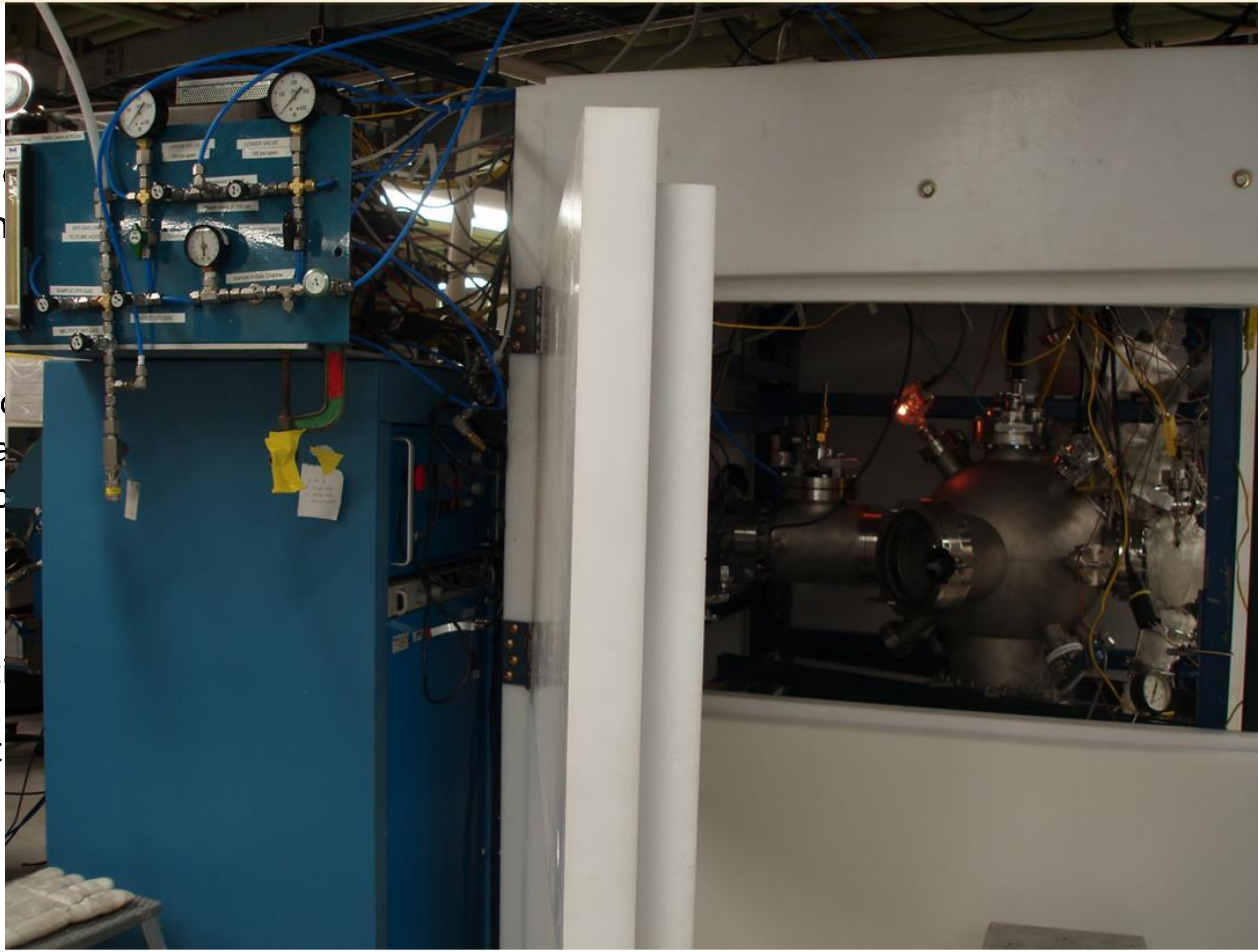
SPECIMEN DESIGN AND FACILITY

Specim
hold th
medium

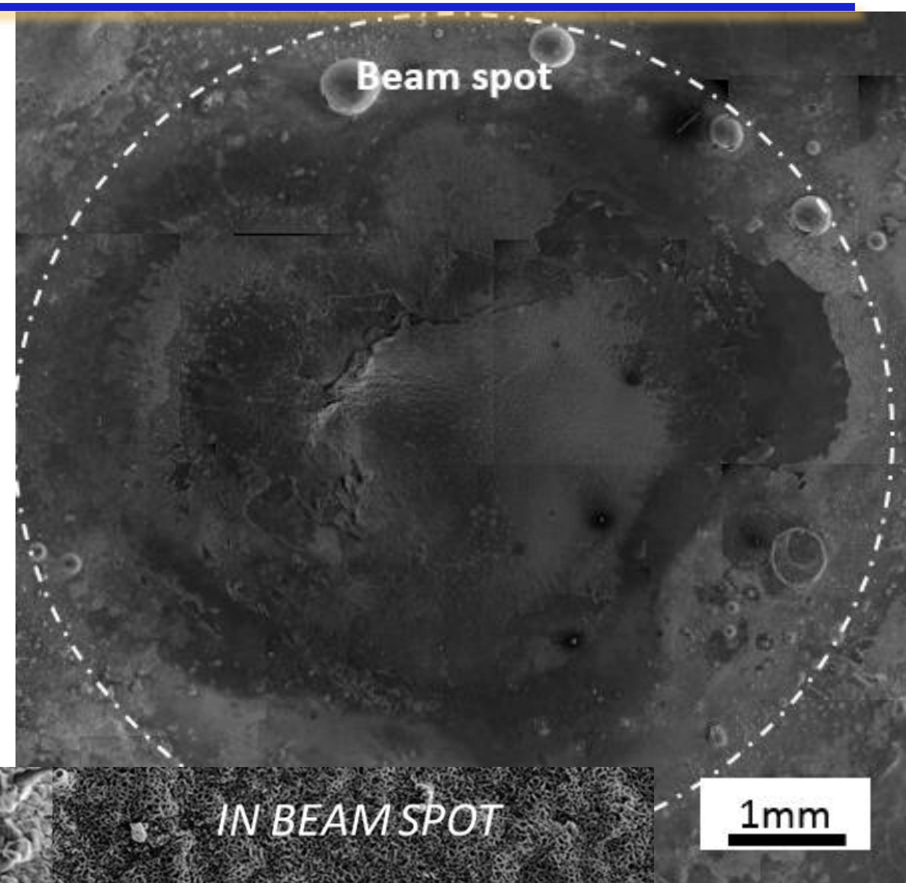
Do
va
sp

Preparat

Schemat



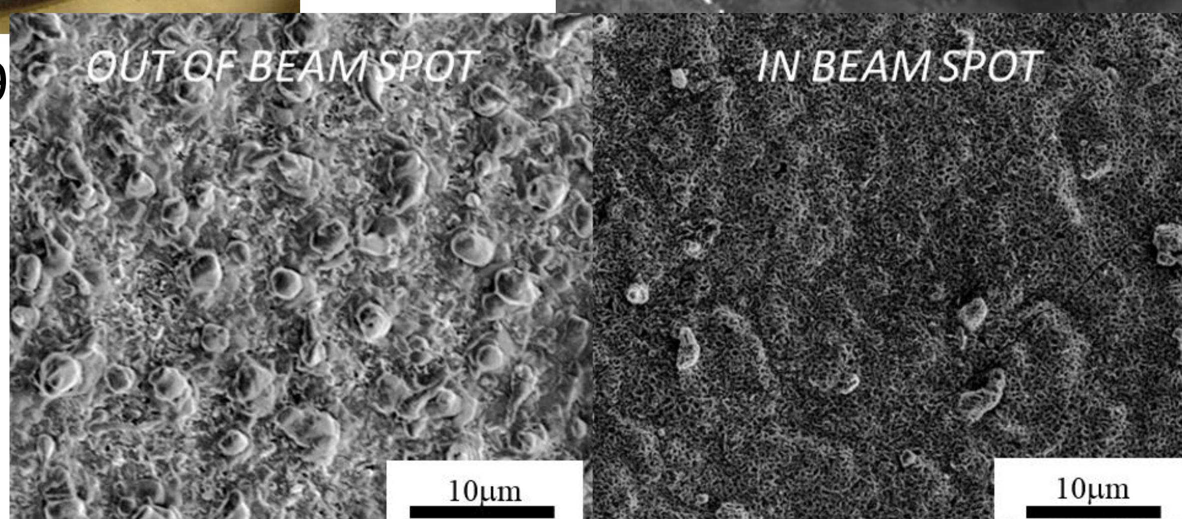
INITIAL INVESTIGATION OF ICE SAMPLE



LBE Side on HT-9

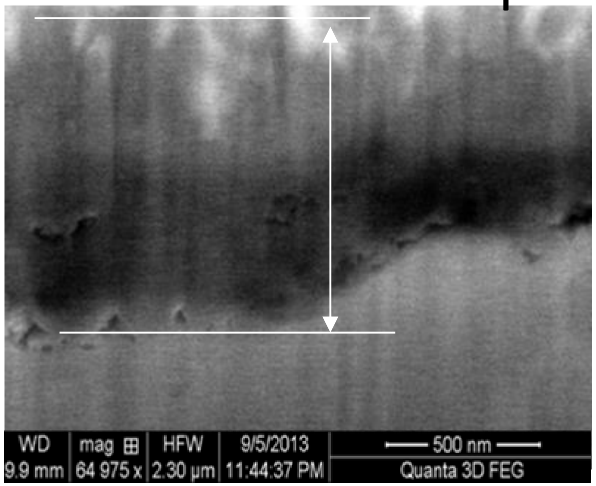
~60 hours

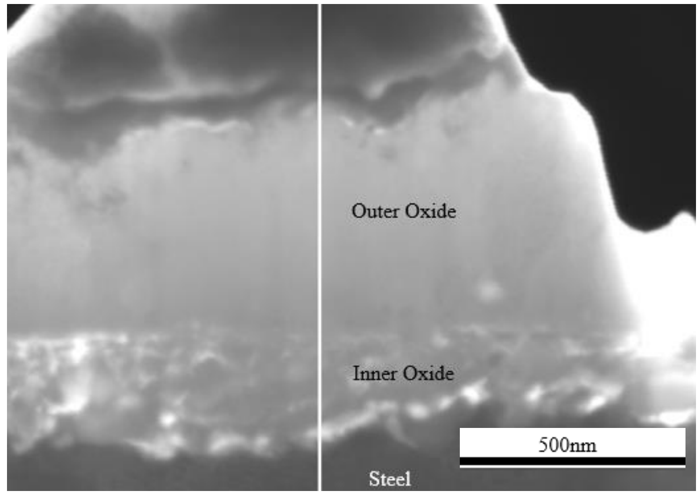
430C, 2.5dpa

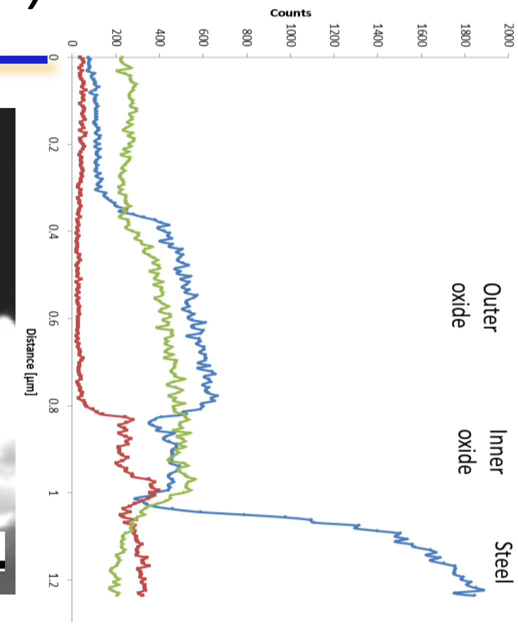


STEM ON ICE SPECIMEN (HT-9)

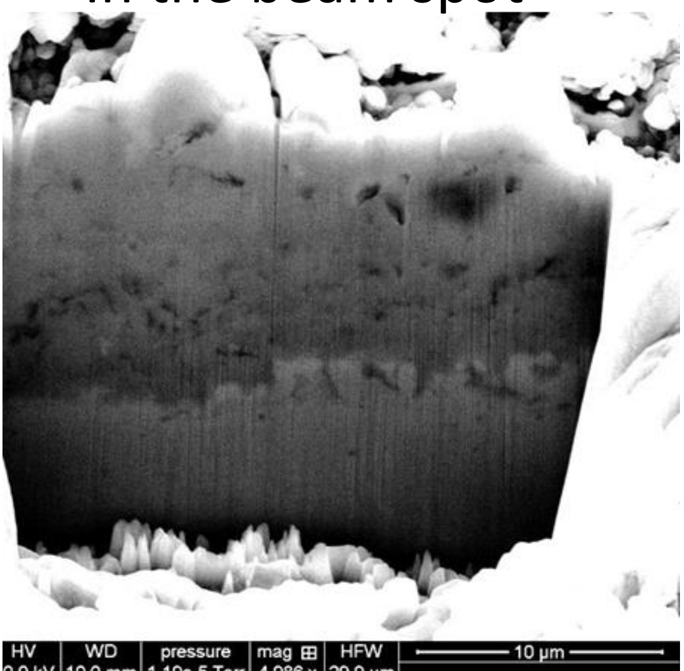
Out of the beam spot

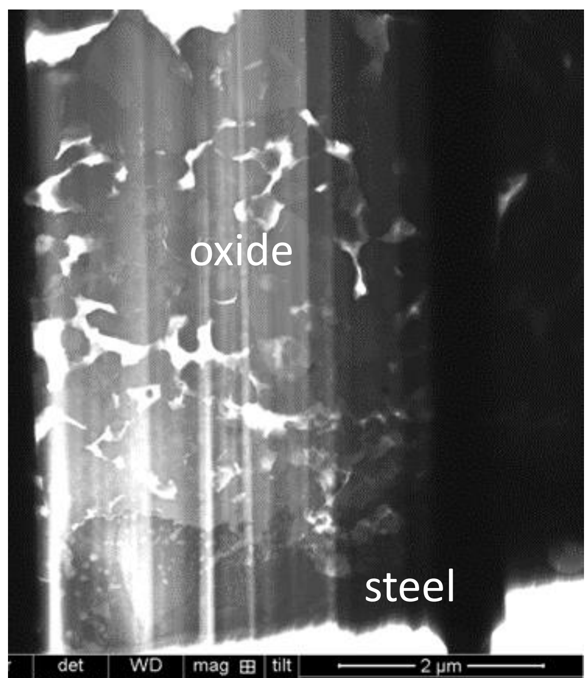






In the beam spot





The ion beam irradiation enhances the oxidation significantly and leaves lesser dense oxides on the sample surface

SUMMARY

- Introduction to selection of heavy liquid metals in CSP and nuclear applications.
- Significant synergistic problems between the different engineering applications.

- Phenomenon LM corrosion and structural materials selection

- Oxide layer formation on austenitic and ferritic stainless steels as well as Fe-Cr-Al alloys in LM static and flowing conditions.
    - -flow of 3.5m/sec is acceptable.
    - -low oxygen content fosters the development of ferrite zones in austenitic materials
    - -Fe-Cr-Al shows better corrosion properties at higher temperatures.

- Adherence of oxides on the substrate material can be sampled directly.

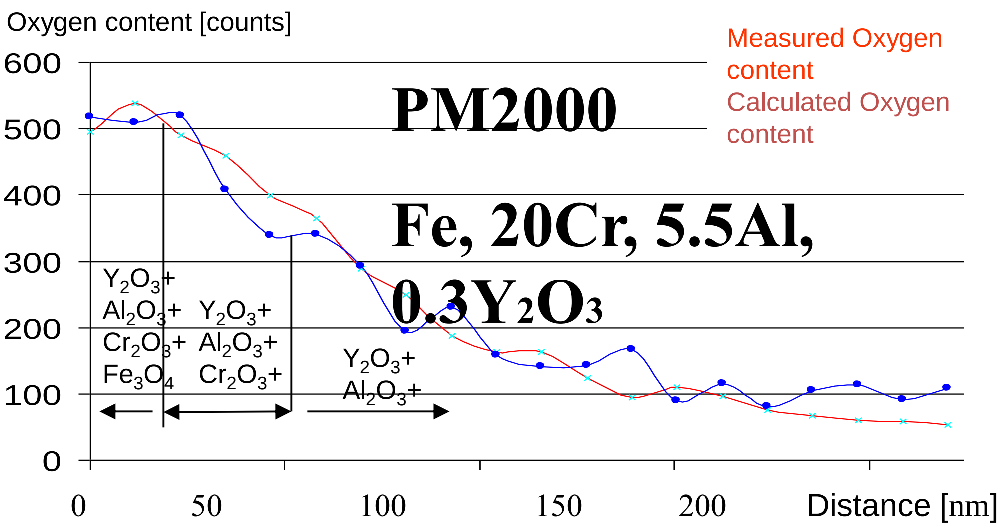
- Introduction to the ICE experiment.→ accelerated oxidation in the beam spot.

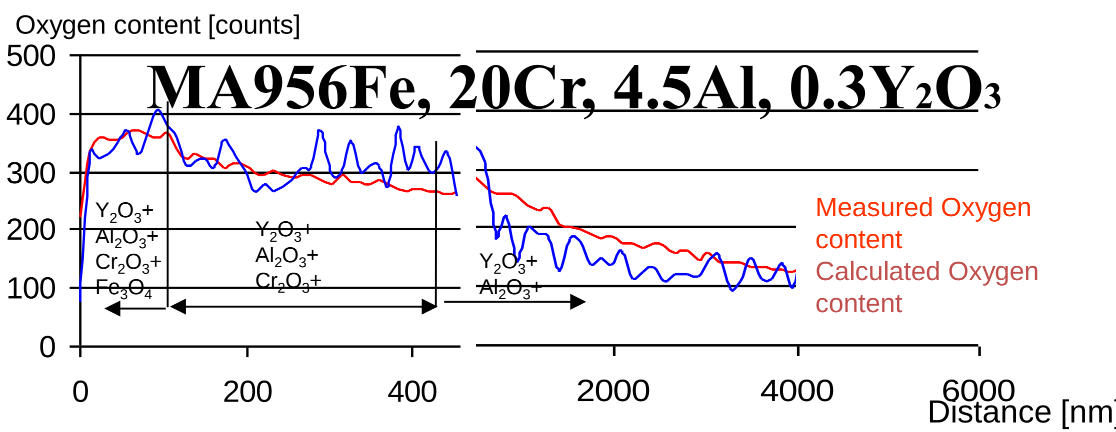
Thank you for your attention!

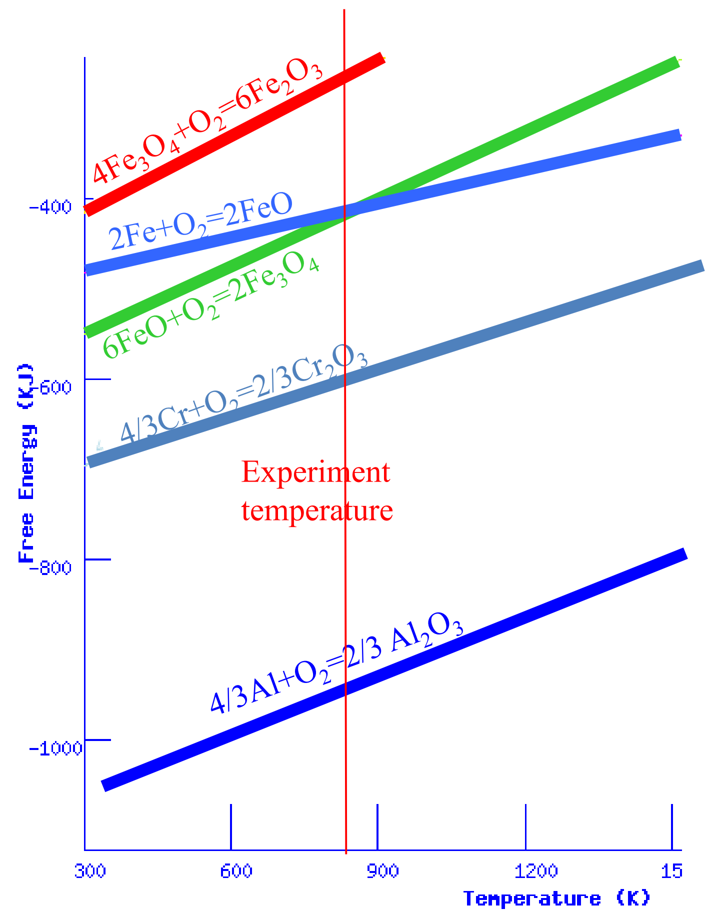
SunShot
U.S. Department of Energy

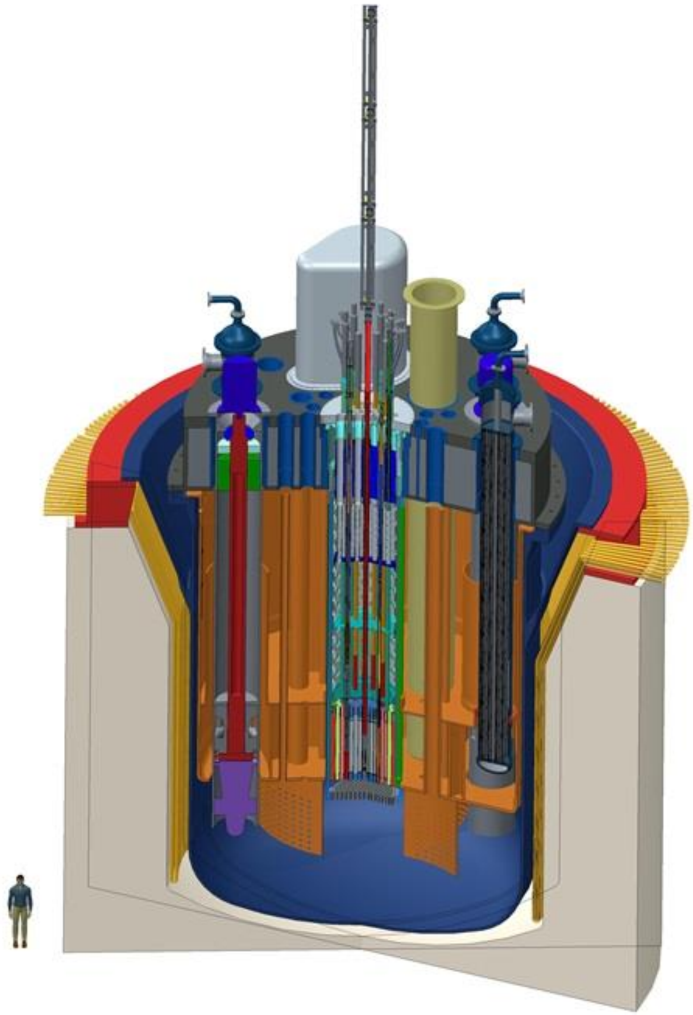
OXIDATION STAGES OF PM2000 in LBE

Based on the published electron binding energy of each element, XPS allows the determination of the oxidation state of the element. Here the measured oxygen in the layer is compared with the calculated oxygen for the material.

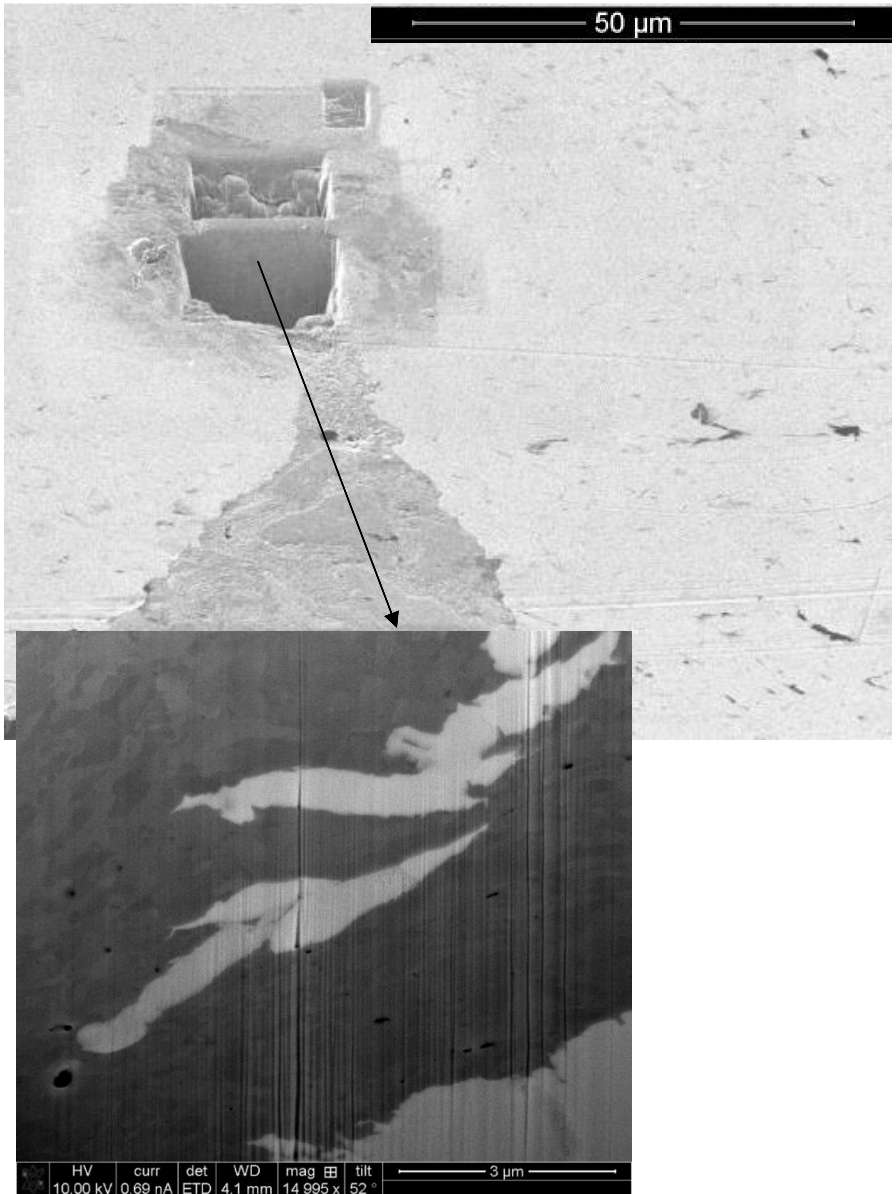


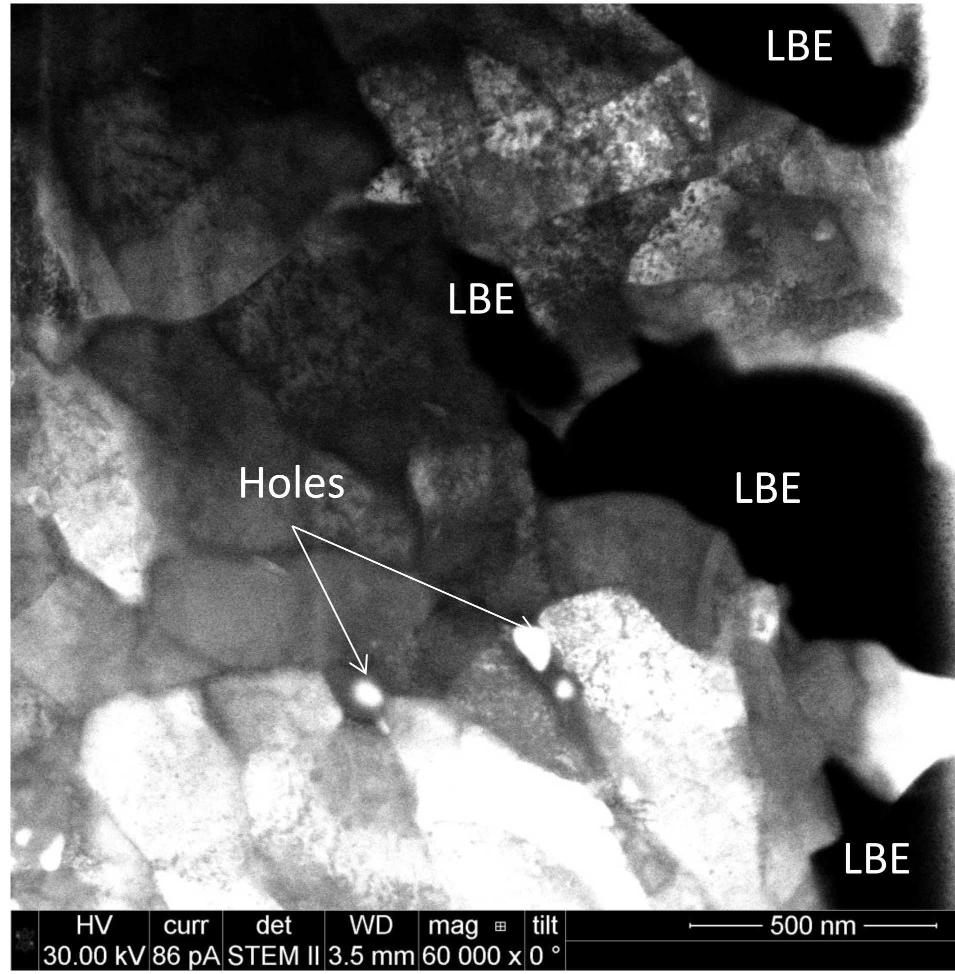






FIB PROCESSING AND STEM ON LME TEST SAMPLE (T91); SCK SAMPLE

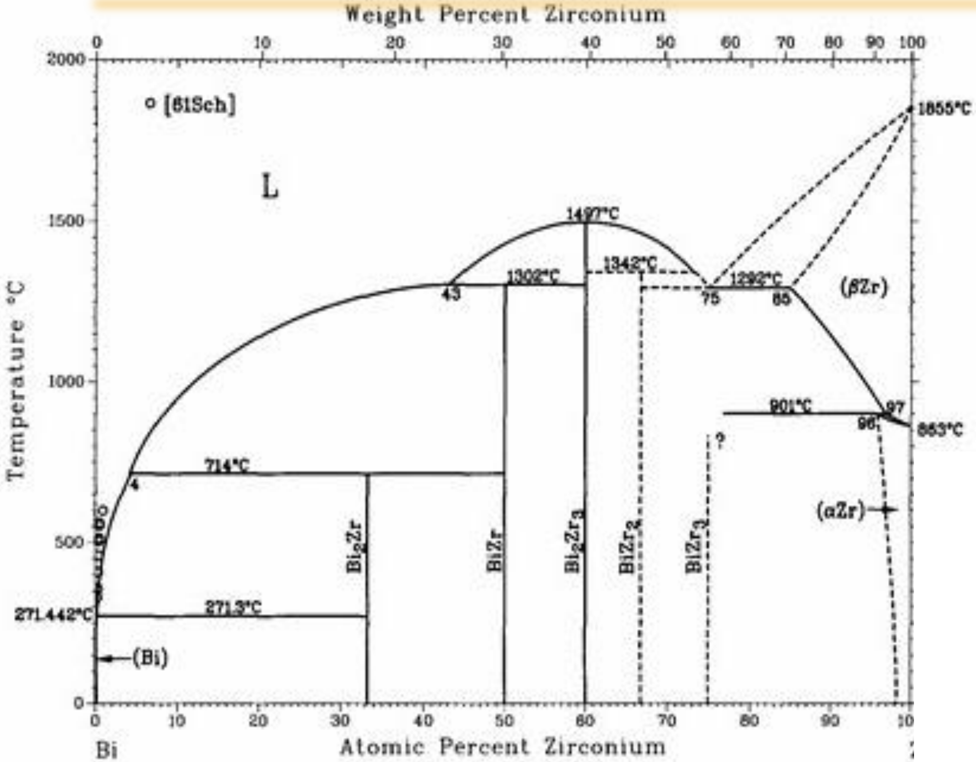




In collaboration with E. Stergar, SCK

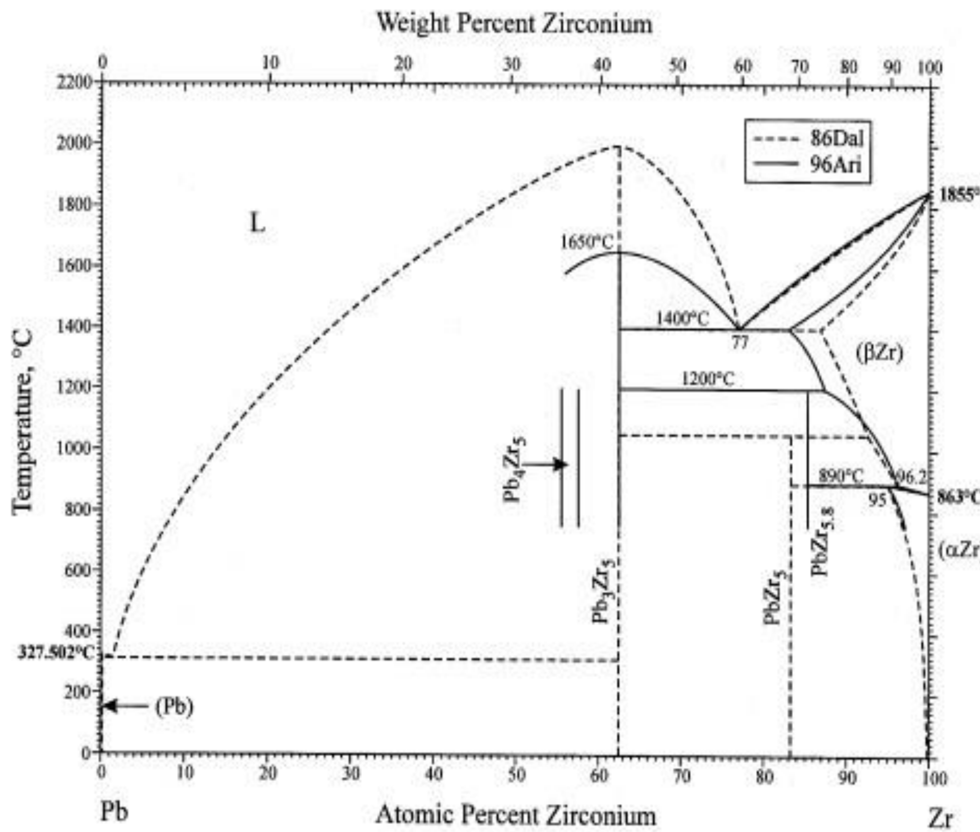
LBE penetrates at GB

Since in an encapsulated system no new oxygen supply is possible intermetallics may form



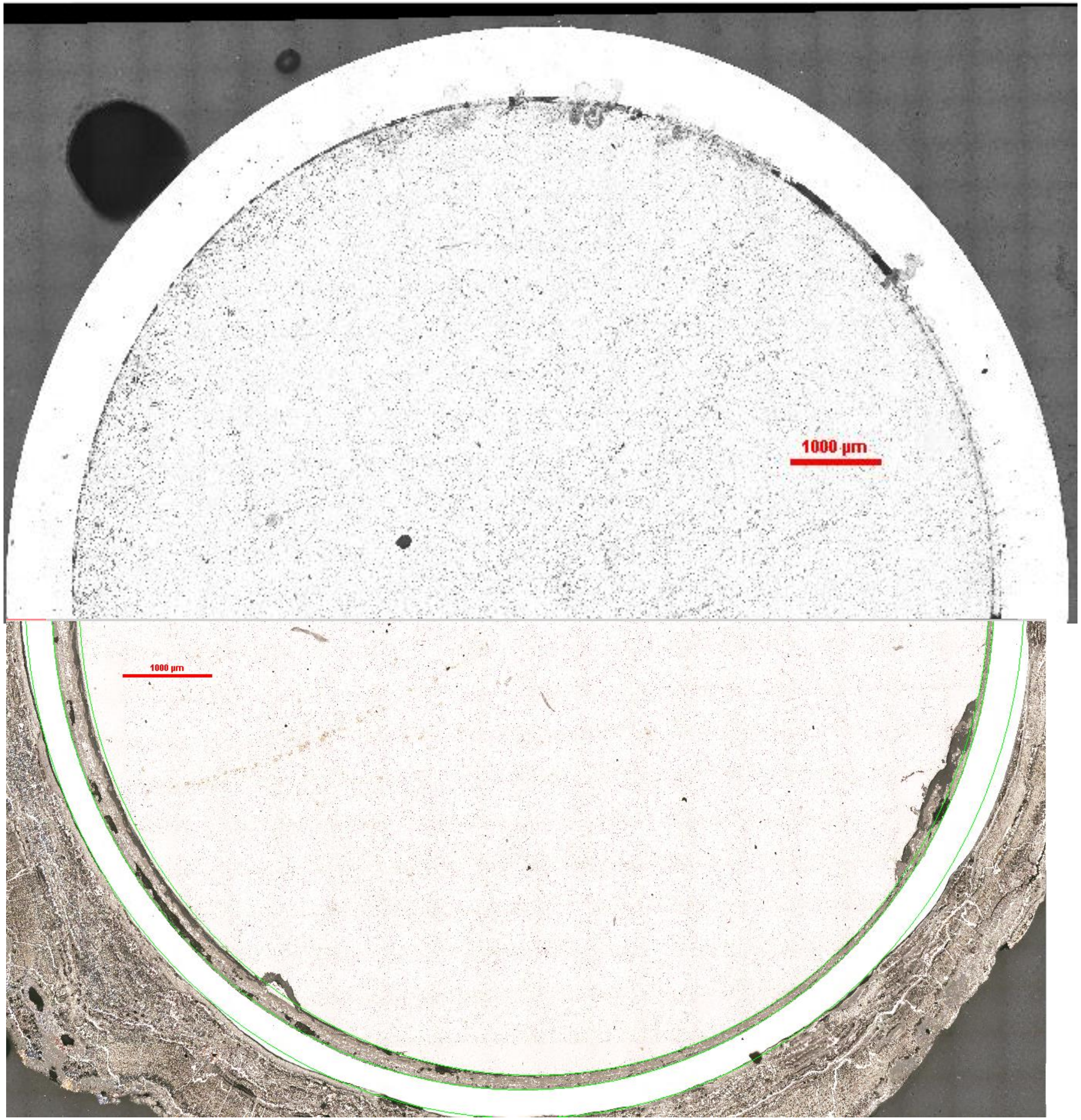
A large number of intermetallic phases can be formed between Bi, Pb and Zr.

While no ternary phase diagram is available the binary systems show significant formation of intermetallic phases



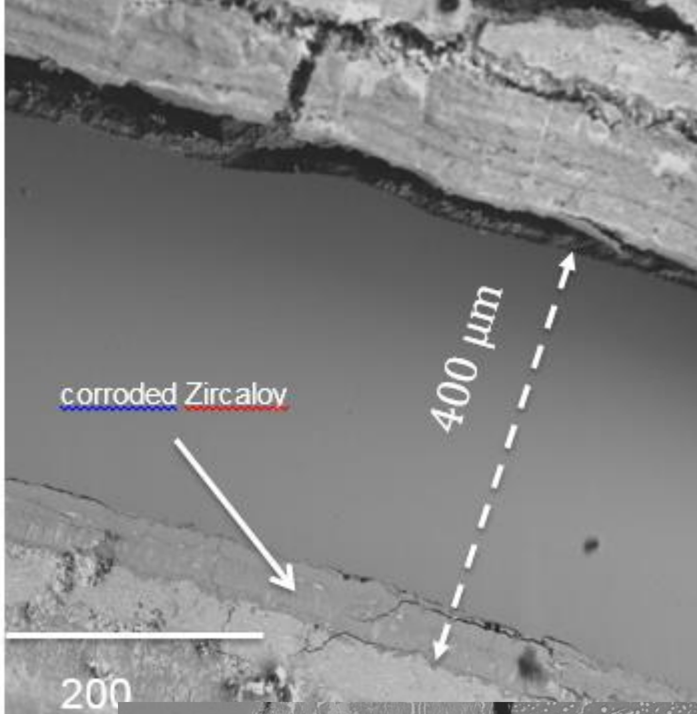
The pre-irradiation tests did show that LM-Zr cladding is not a concern due to passivation layers formed and constant fresh supply of oxygen.

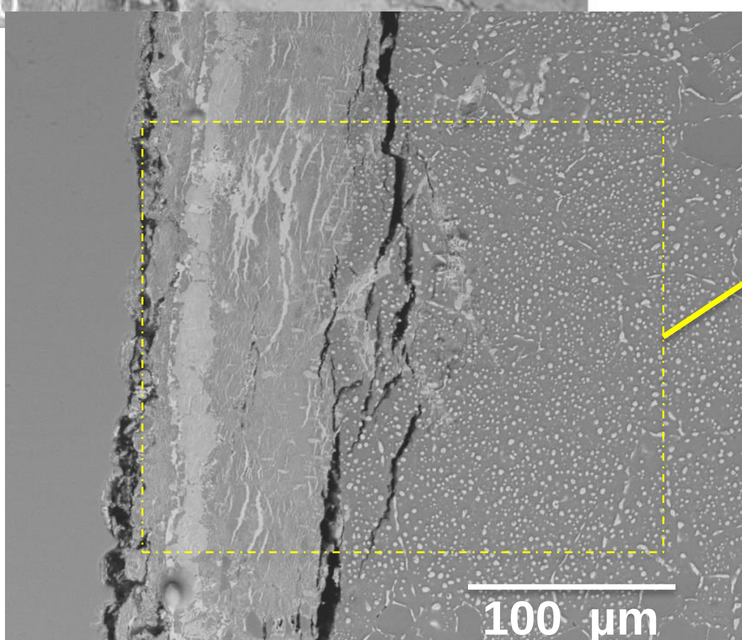
OM comparison (capsule 1)

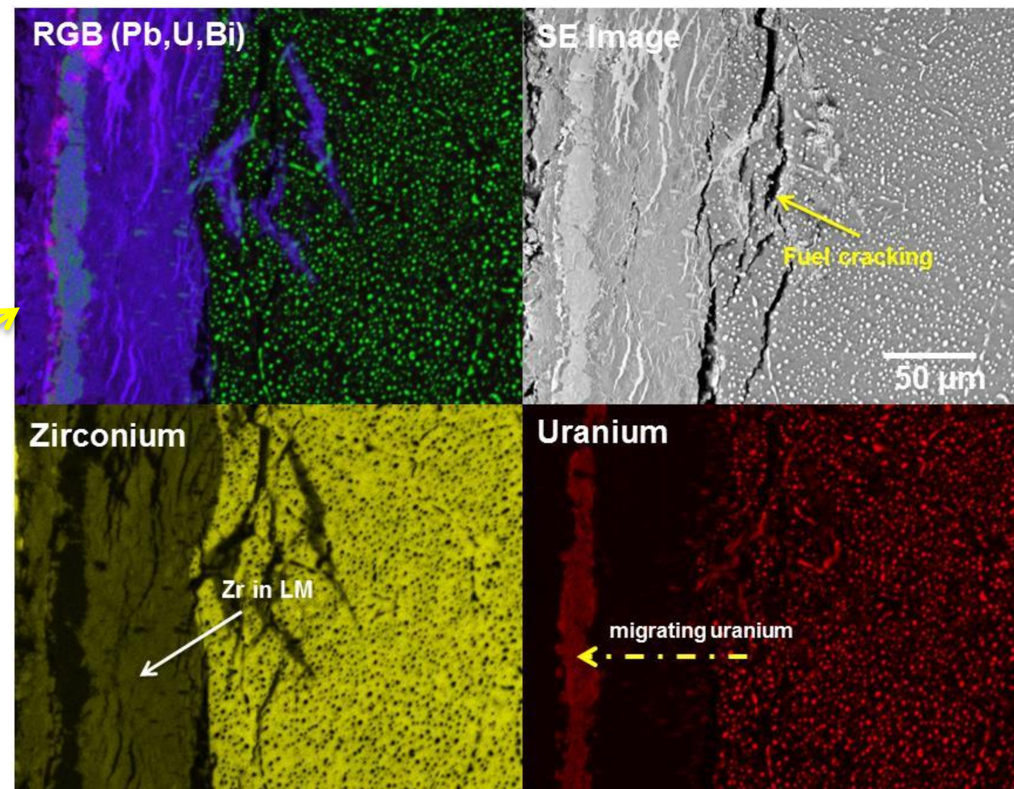


SEM OF THE IRRADIATED CAPSULE 1 SAMPLE

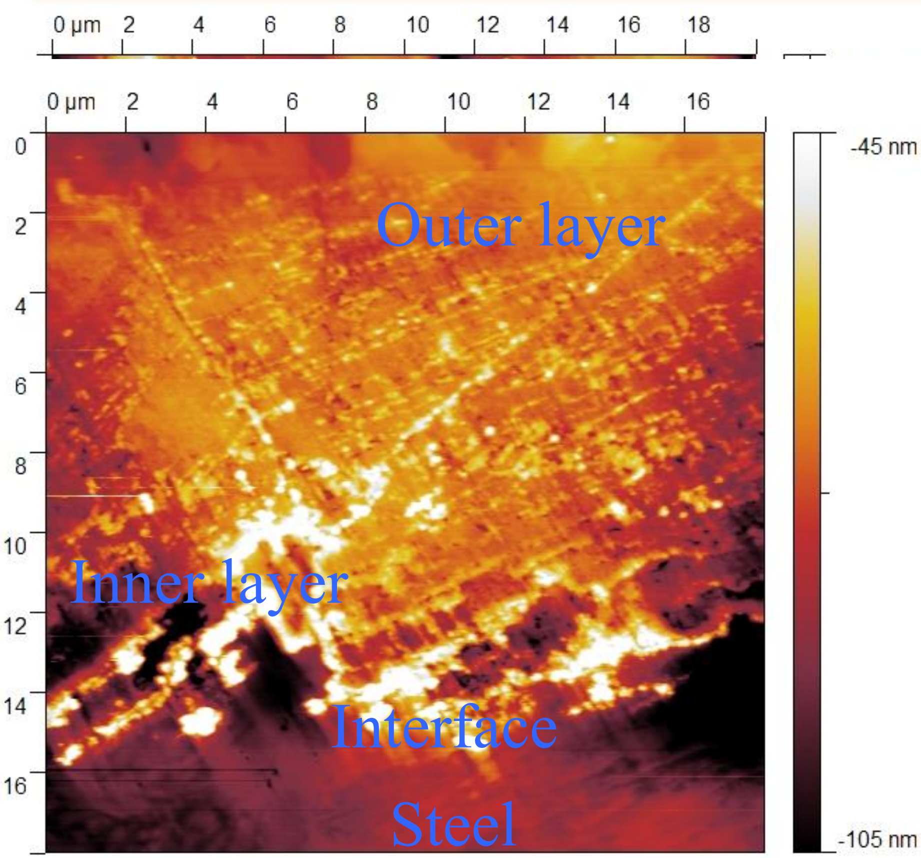
- Zr in the LM,
- Some U is found at the Zr interface.
- Cracks in the LM?
- Multi phase mixtures in the LM

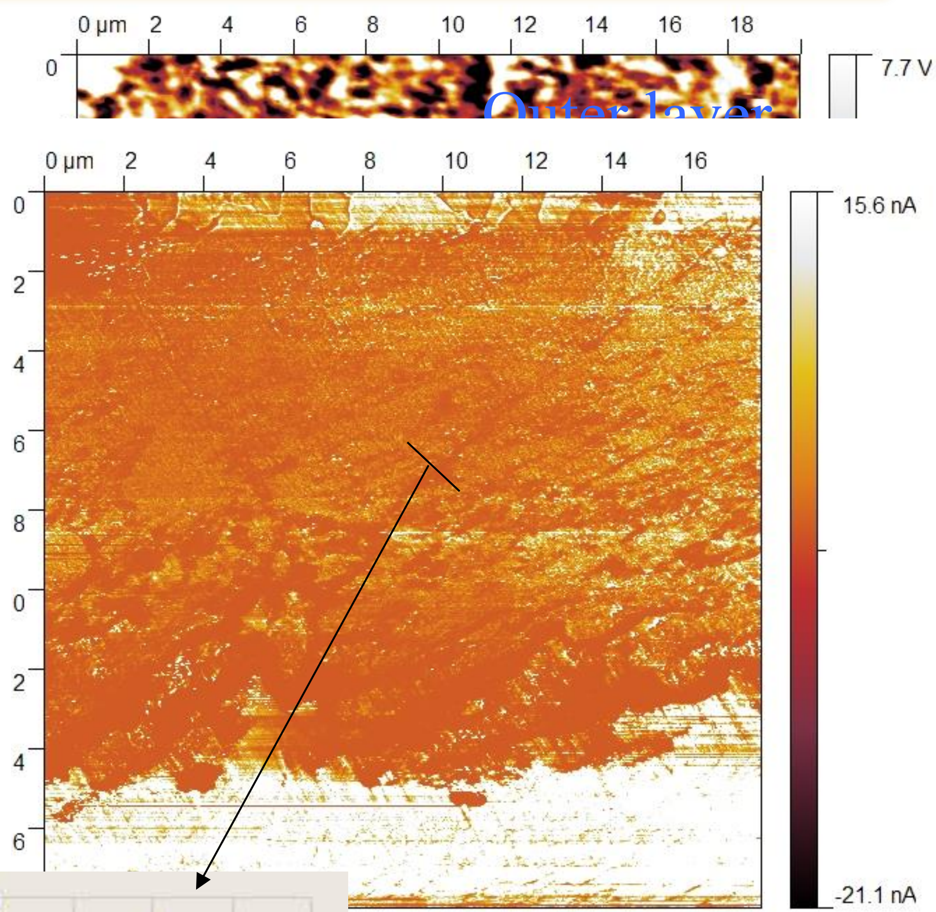




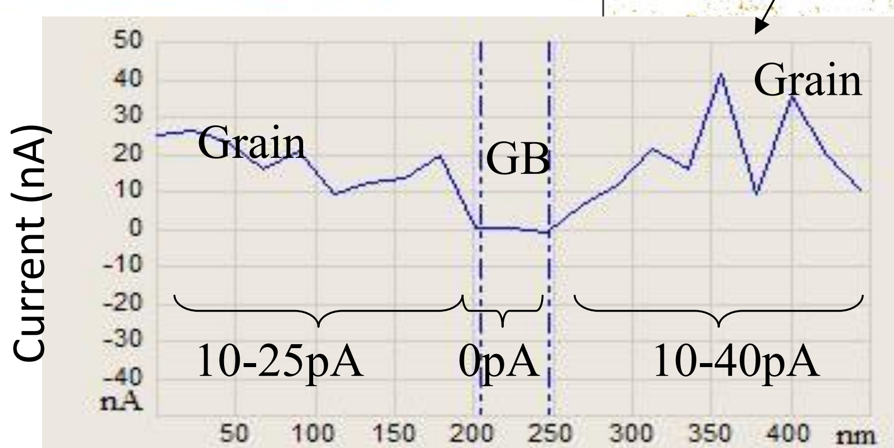


AFM/MFM/C-AFM ON HT-9





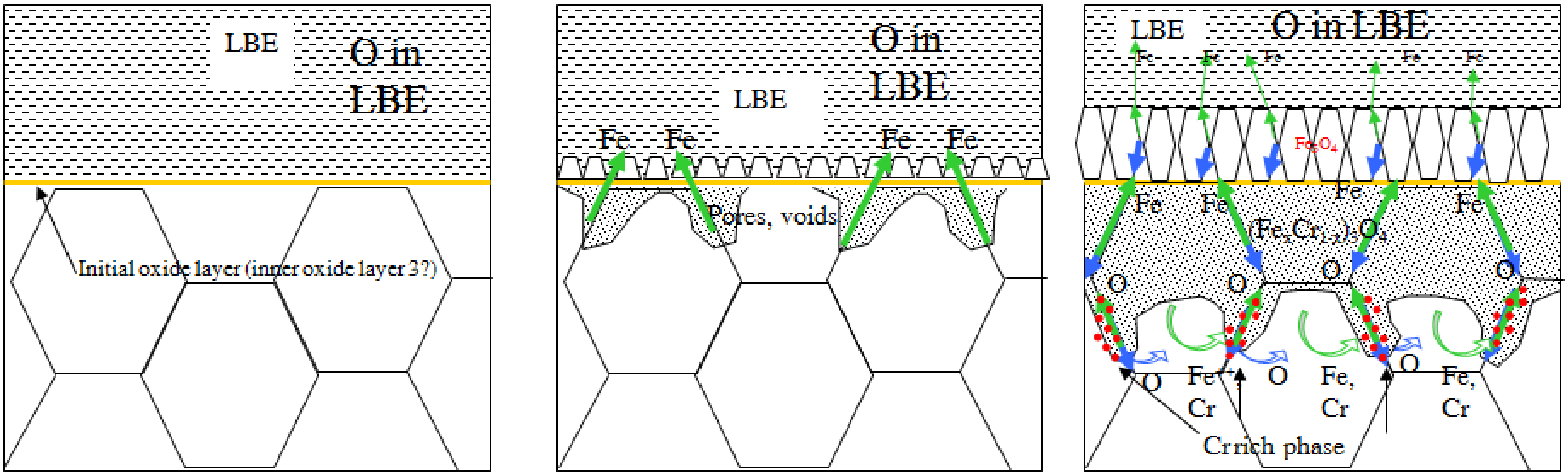
Cr_2O_3 lower electrical conductivity than Fe_3O_3



Current line profile through the boundaries identified

HOW DOES THIS OXIDE LAYER FORM in a Ni containing materials IN LIQUID METAL?

Oxide layer growth: leaching and oxidation takes place:



P. Hosemann, et al. *J. Nucl. Mat. 375, 3, 30 (2008)323-330*