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Title: The Irradiation and Corrosion Experiment (ICE2) ~~Comparison of corrosion in HT-9 in contact with static 500 C LBE with and without simultaneous 6 MeV proton irradiation~~

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Comparison of corrosion in HT-9 in contact with static 500 C LBE with and without simultaneous 6 MeV proton irradiation

S. Qvist, M. Caro, A. Bolind, Y. Wang, M. Bourke, P. Hosemann

A major unknown in the development of materials for advanced nuclear systems is related to the question of corrosive materials degradation under "in-service" operating conditions. In this work, we describe the irradiation/corrosion experiment, namely ICE*, performed at LANL within the Los Alamos National Laboratory – University of California Berkeley (LANL-UCB) collaboration. The purpose of this work is to study synergistic effects of irradiation on steel corrosion, and investigate if and how a steady state concentration of defects continuously created by displacement cascades affects surface chemistry such as oxidation or dissolution. ICE* builds-up on the experience gained in a previous ICE-1 experiment, where HT-9 steel was exposed to proton irradiation in the presence of Lead Bismuth Eutectic (LBE) at high temperature. ICE* constitutes a natural continuation with improved capabilities, i.e. monitoring Oxygen content in LBE, ability to reach higher temperatures and dose values.

THE IRRADIATION AND CORROSION EXPERIMENT (ICE2)

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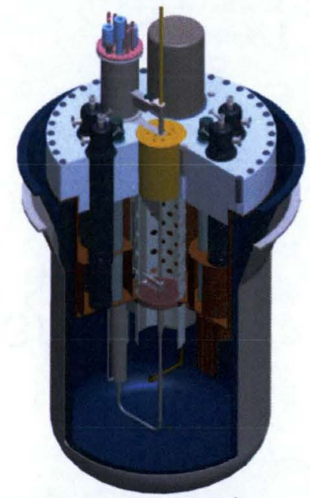
LBE as a nuclear coolant and/or spallation neutron source

Opportunity

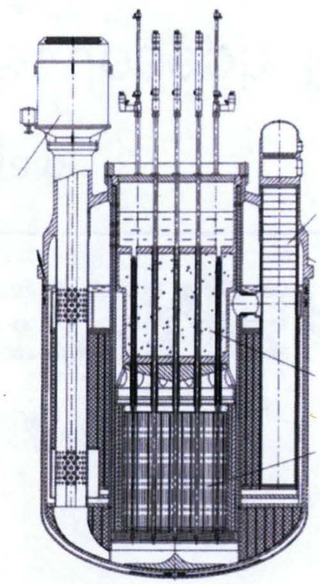
Excellent neutron yield
Low neutron reaction cross sections
Low melting point
Excellent thermal properties
Can not be radiation damaged

Challenge

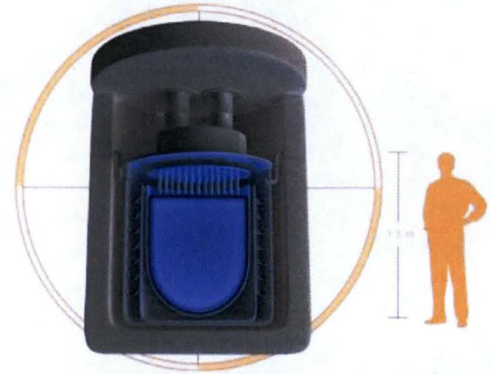
<u>Highly corrosive to steel</u>
Liquid Metal Embrittlement
Liquid Metal Enhanced Creep



XT-ADS, EU



SVBR-75, Russia



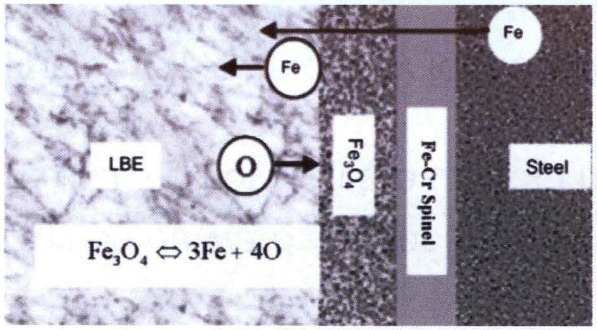
Hyperion, US

HT-9 steel corrosion in LBE

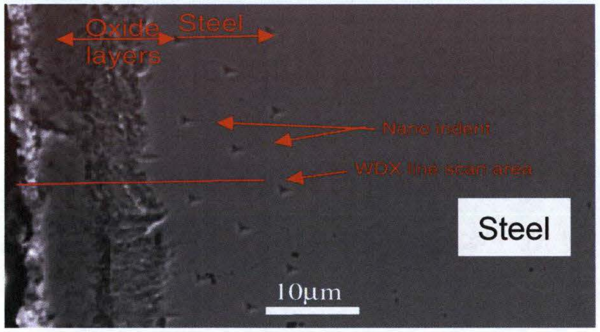
Non-irradiated condition

- Experiments show the formation of a double oxide layer structure: 10 μm thick after 600 h at 535 °C (Fe_3O_4 magnetite and $FeCr_2O_4$ spinel oxides)

Schematic representation of corrosion mechanism in LBE



J. Zhang, N. Li, J. Nucl. Mater. 373 (2008) 351



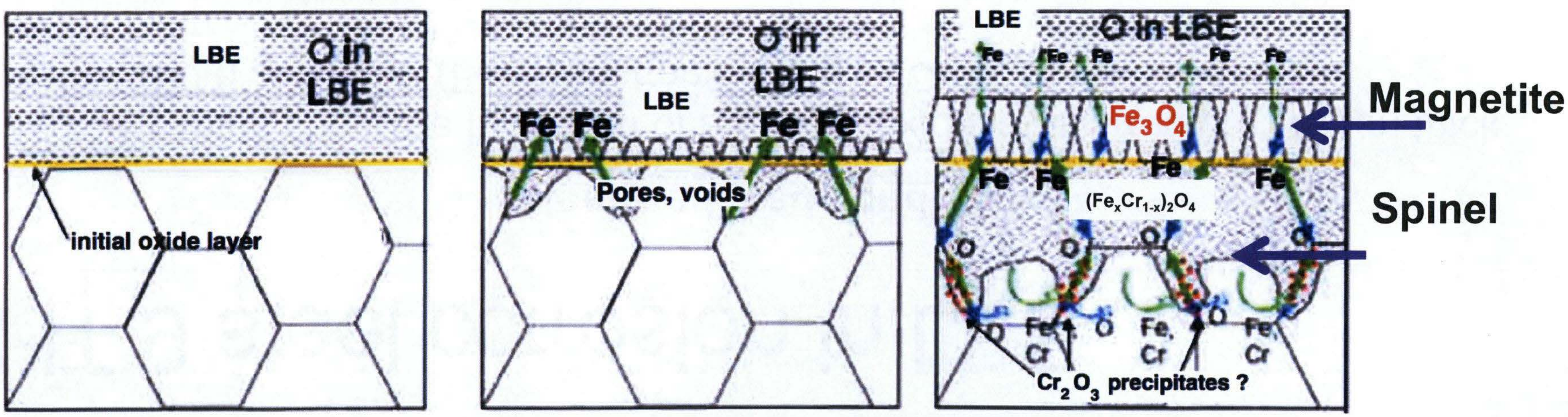
SEM image of HT-9 exposed to LBE corrosion *DELTA LOOP - LANL*

P. Hosemann et al., J. Nucl. Mater. 377 (2008) 201

- Structure of oxide layers formed on steels is influenced by several factors:
  - Steel composition, temperature, oxygen content in LBE, LBE flow velocity, initial impurities in the steel and LBE coolant, etc.

Corrosion model

- Formation of multi-phase oxide scales is due to different diffusion rates in alloying components:
  - Fe diffusion outward: Surface growth of the outer magnetite layer, **Fe_3O_4**
  - Inward diffusion of O in the LBE: O reacts with Fe and Cr leading to the formation of Fe-Cr spinel **$(Fe_xCr_{1-x})_2O_4$**
  - Cr diffusion is slower: Only found in the inner layers leading to Cr_2O_3 precipitates

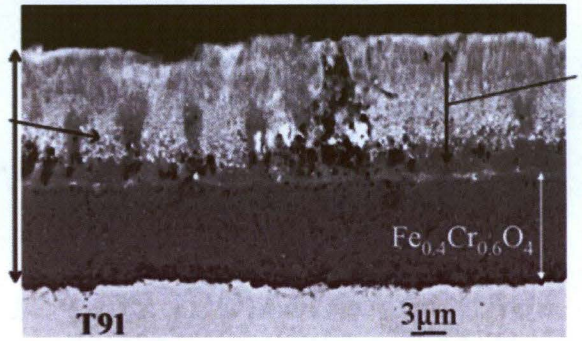


Glasbrenner, et al., J. Nucl. Mater. 296 (2001) 237
P. Hosemann, priv. comm. (2011)

Corrosion protection

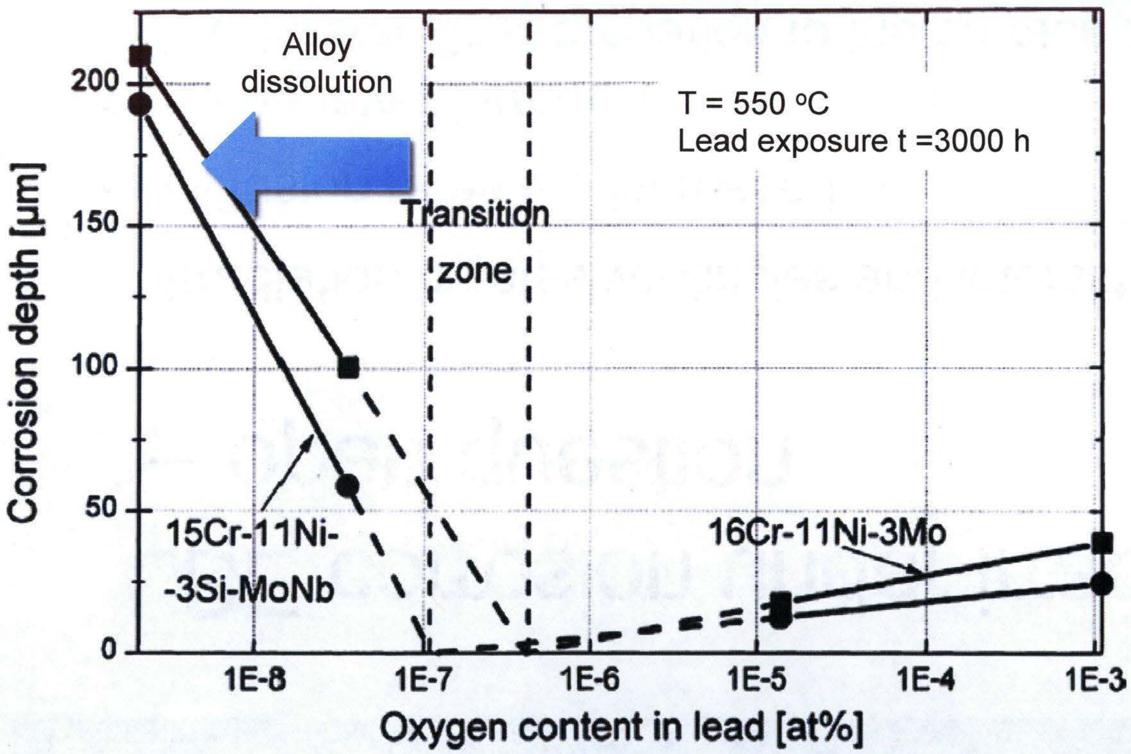
Requirement for protection - Stable, dense, adherent oxides

Porosities in magnetite: Lead penetrations 20 μm



Martinelli et al., Nucl. Eng. Des. 241 (2011) 1288

Effective oxide layers are formed by controlling LBE oxygen concentration



Significant corrosion reduction in austenitic steels at oxygen contents in lead above 10^{-6} at.%

I.V. Gorynin et. Al, Proc. HLMC-98 1 (1998) 190

LBE corrosion under irradiation – open question

1. Irradiation creates vacancies and interstitials
2. Diffusion rates are increased
3. Oxide layer formation could be affected
   A. Faster Cr segregation to the surface leading to a more protective oxide scale
   B. Enhanced ion transport through the passive film leading to enhanced corrosion
   C. Change due to irradiation not important/noticeable

- A, B or C? Cumulative dpa vs. dpa-rate?

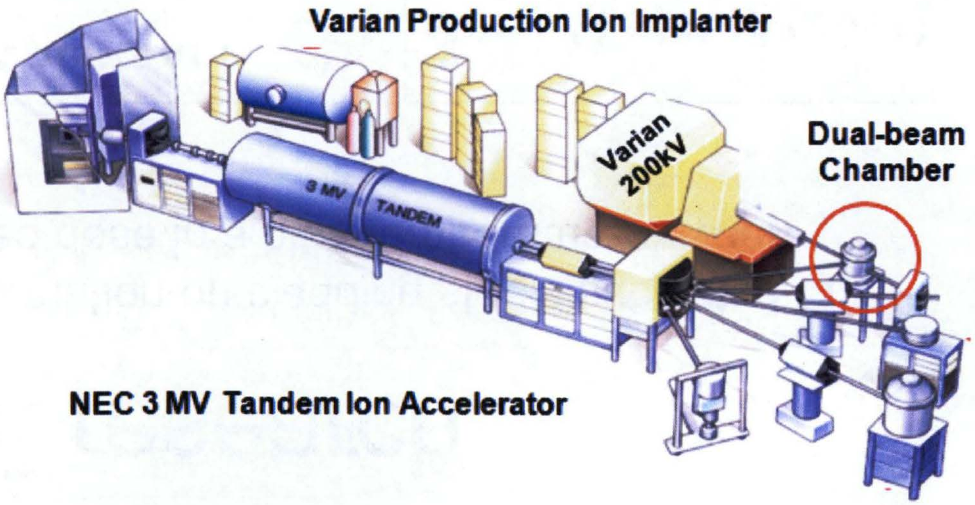
ICE2 in US LBE research

ICE2 aims to investigate oxide formation on cladding steels subjected to irradiation with a range of received dose in a high temperature oxygen controlled LBE environment.

US LBE material compatibility tests for commercial deployment	**Current status (2011)**
Static LBE, temperature + oxygen control	Done (many tests)
Static LBE, temperature + irradiation	Performed at **LANL:** ICE1 Insufficient dpa* and °C
Static LBE, temp. + oxygen control + irradiation	ICE2
Flowing LBE + oxygen control	Performed at **LANL:** DELTA loop Insufficient m/s flow
Flowing LBE + oxygen control + proton irradiation (+ tensile stress)	ICE3? (future)

Benefits of ion beam facilities

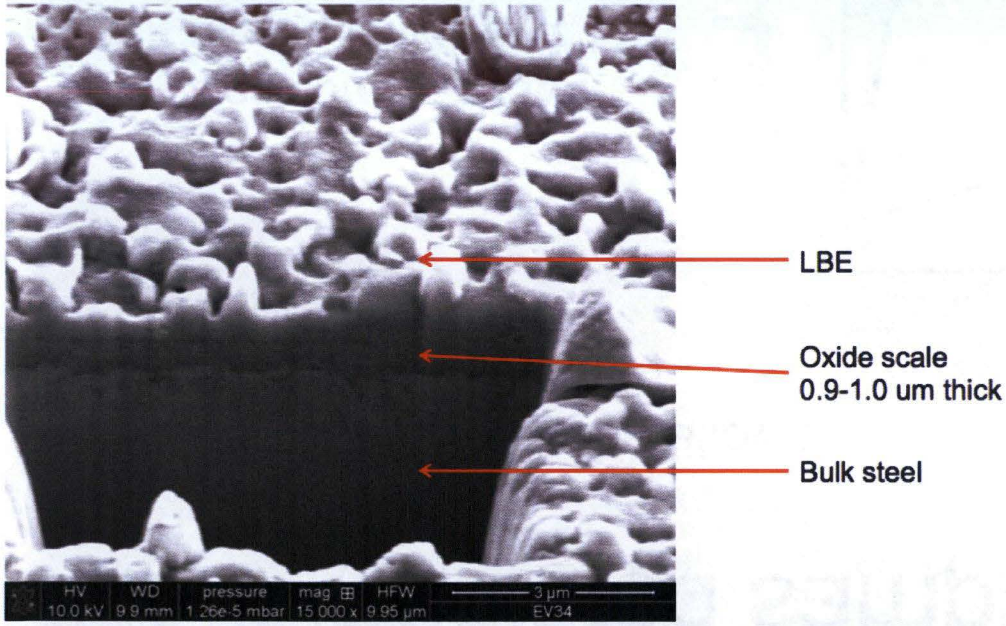
Ion Beam Materials Laboratory (IBML) enable testing of the combined effect of radiation, high temperature, Helium accumulation, corrosive medium, stress, etc., with the benefit of low sample activation and immediate access to post-irradiation experiments (PIE)

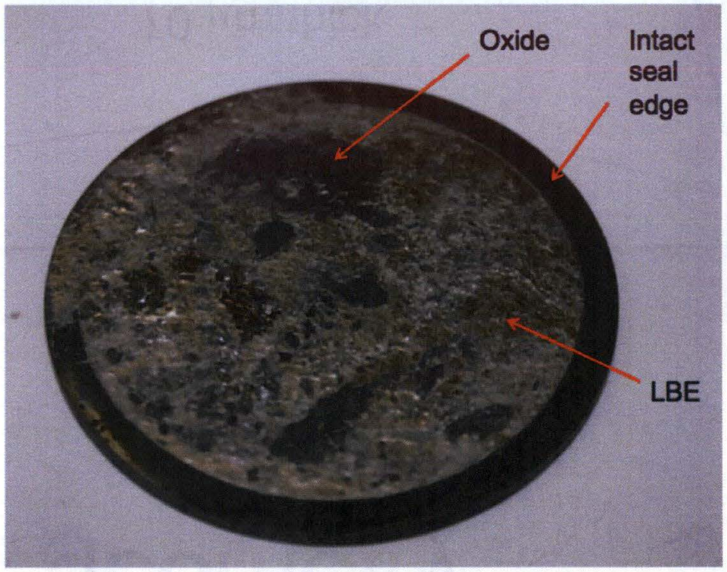


ICE2 initial test run – Non irradiated

- 50h continuous run
- T=500°C
- Oxygen content 0.01 - 0.1 ppm

The layering in the sample showed a 1 µm thick oxide layer formed on top of the steel and LBE deposited on top of that



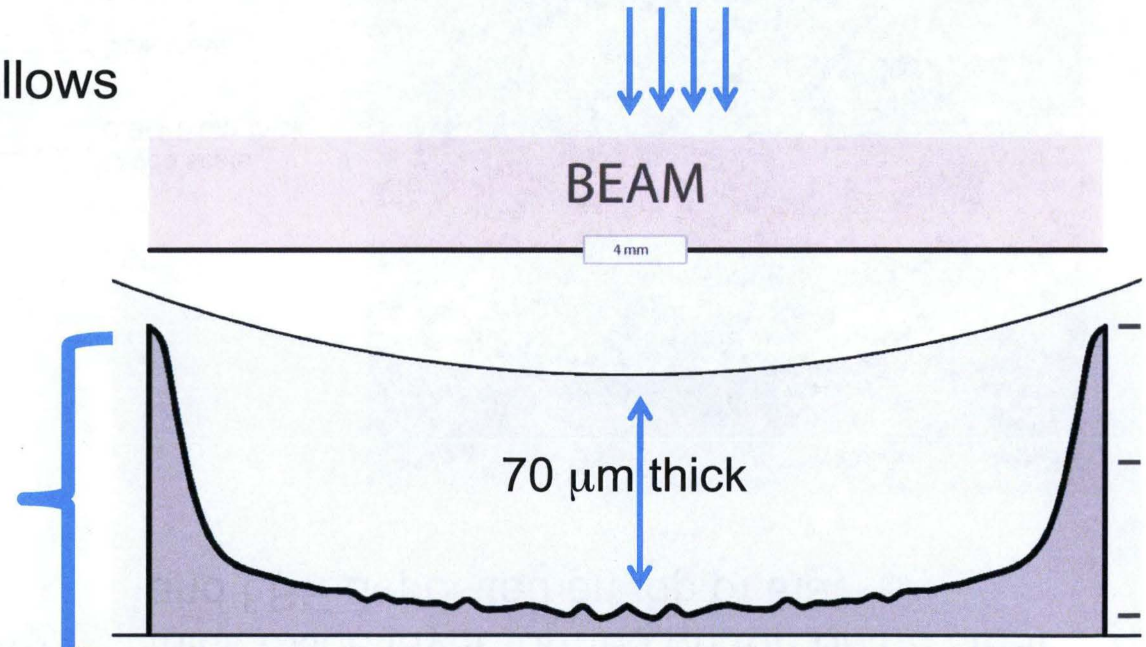


HT-9 specimen layering from trial run, microscope image (right) and optical image (left)

ICE2 Irradiated sample geometry

Specimen concave shape allows analysis after irradiation to different doses

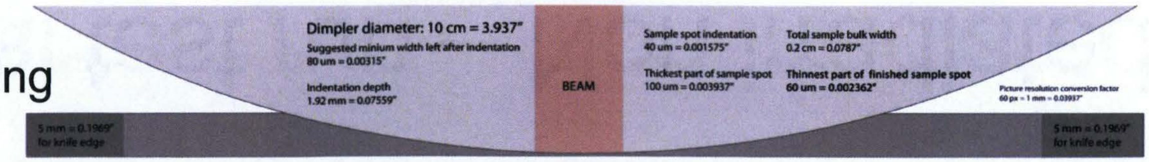
Dose profile shows maximum value at the edges of the specimen



Sample cross section

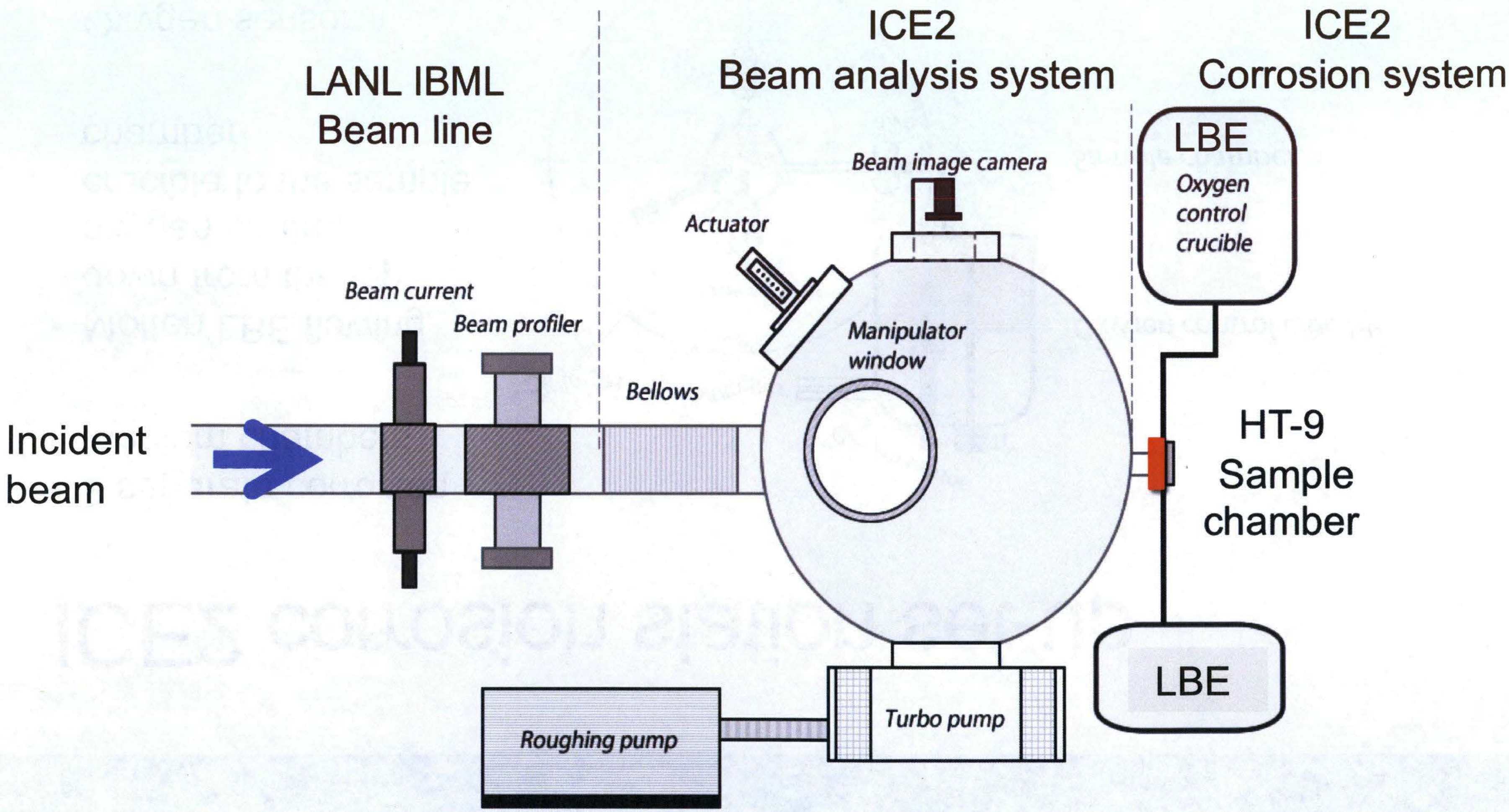
Preparation of HT-9 concave specimens requires thinning of disks *(T. Wynn, 2011)*

Schematic machining



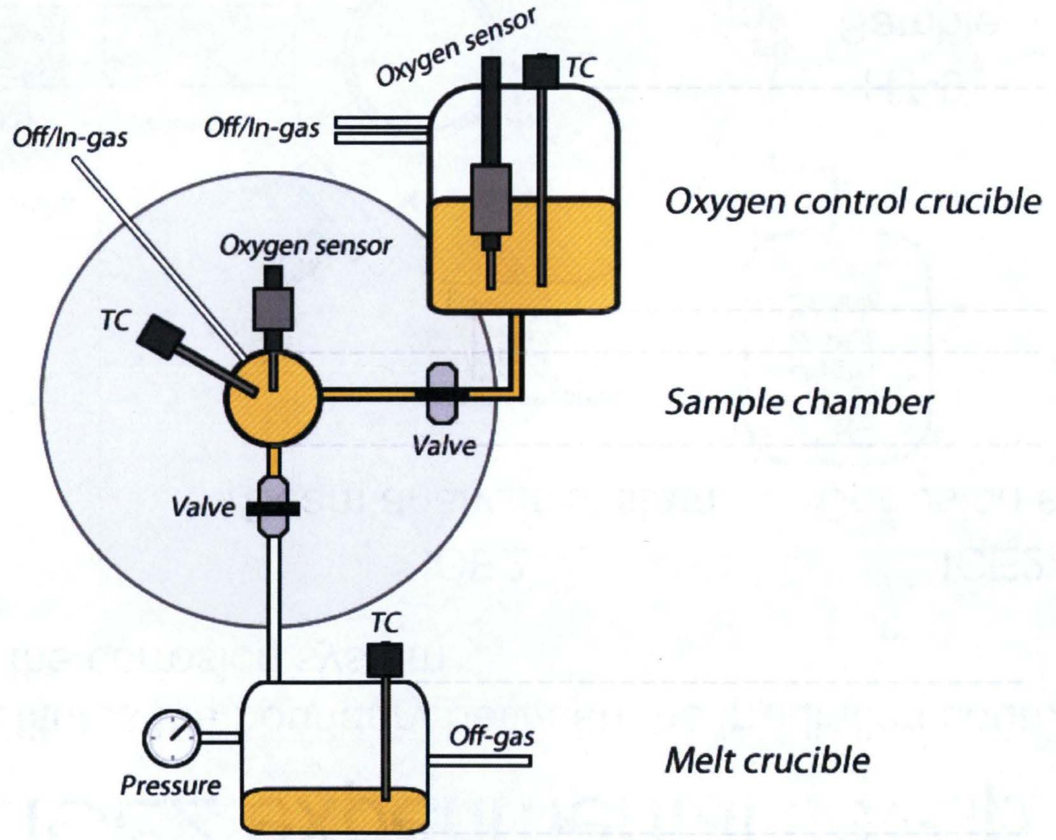
Schematics of ICE2 experimental set-up

- HT-9 specimen itself constitutes the boundary between the irradiation source high vacuum system and the corrosion system

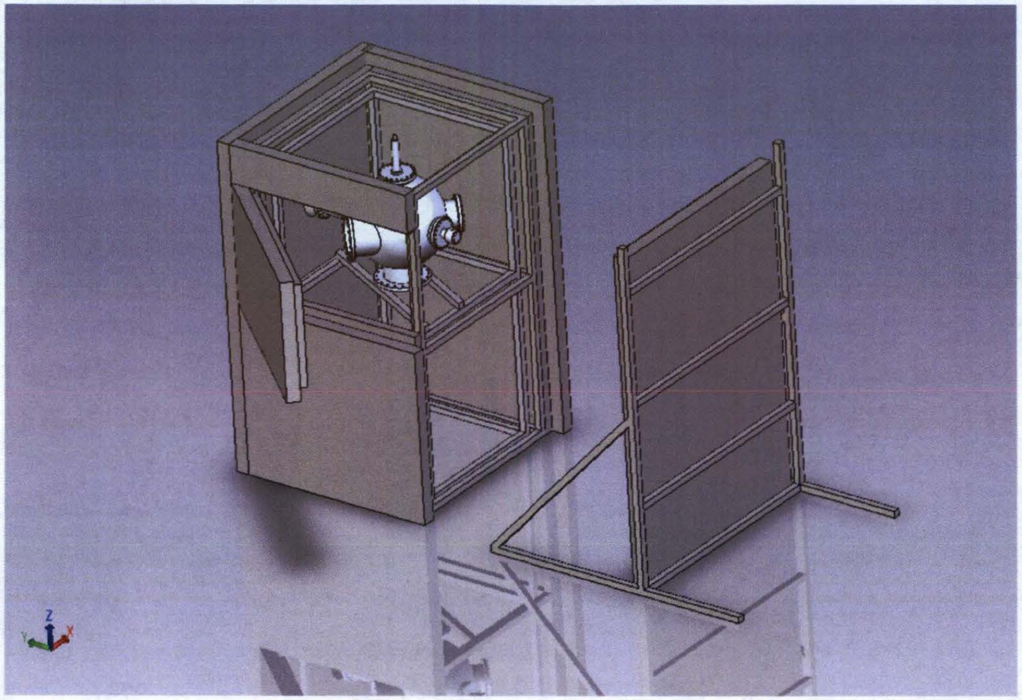


ICE2 corrosion station set-up

- 3 separate corrosion medium chambers
- Molten LBE flowing down from the top oxygen control crucible to the sample chamber
- Oxygen sensor:
- BiO-Yttria (Y_2O_3) used to measure oxygen chemical potential within the melt



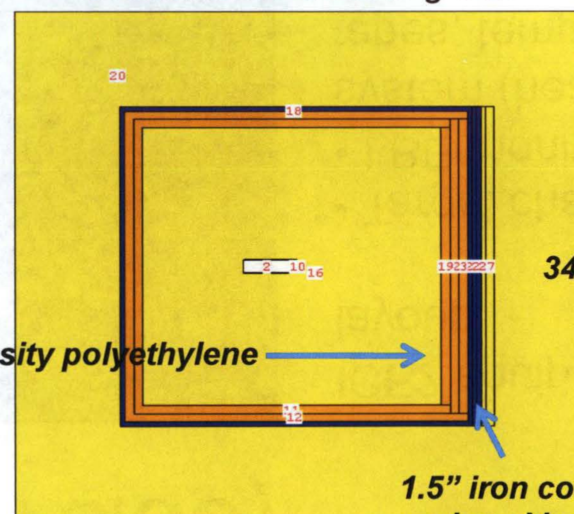
ICE2 station (shielding design)



J. Balog, 2011

Easy chamber access with rolling wall and lateral door openings

MCNPX neutron transport calculations: Shielding box



J. Bliss, 2011

Measured dose at shielding wall ~ 3 mrem/h

Shielding materials : High density and borated polyethylene walls covered with lead blankets

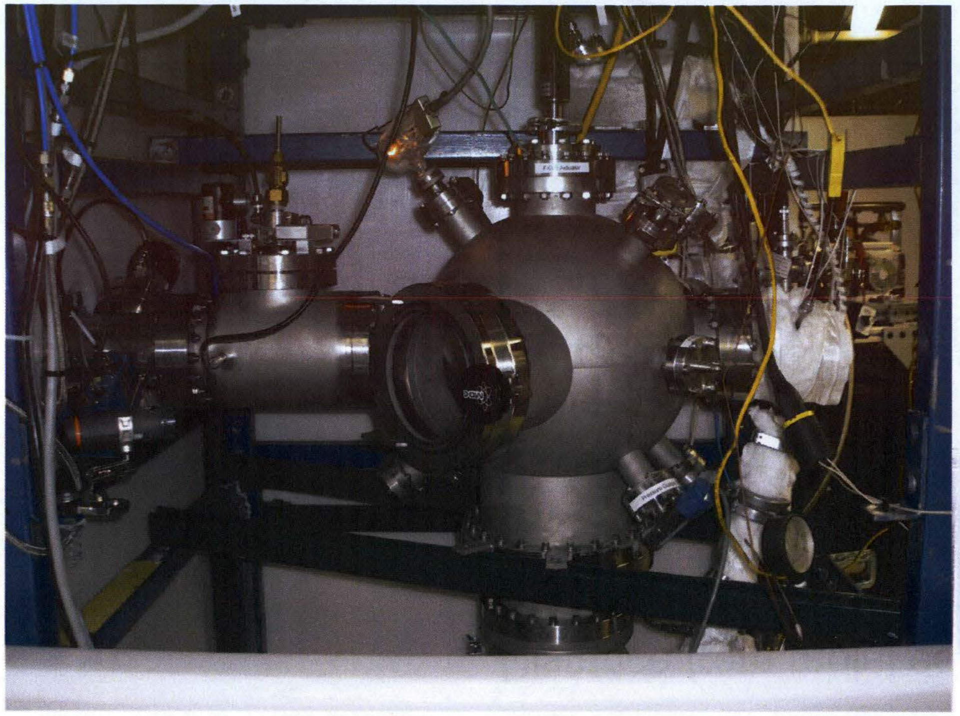
ICE2 station (View from side)

ICE2 equipment layout:

- Target chamber
- LBE monitoring system (heating tapes, temperature and oxygen sensors)
- Radiation shielding box

The chamber is attached to Tandem L-15 beamline

ICE2 chamber and scintillator system

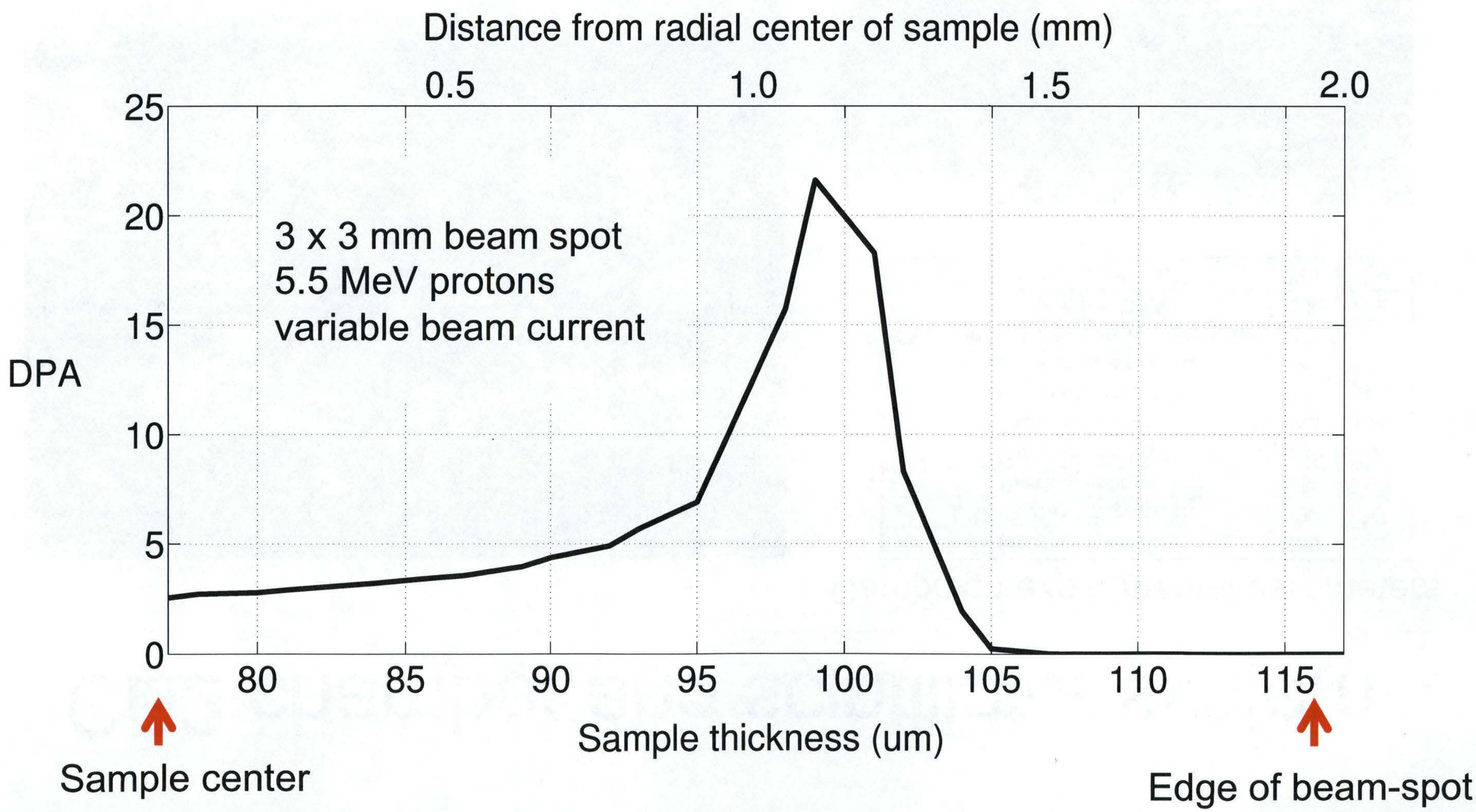


Campaign experimental parameters

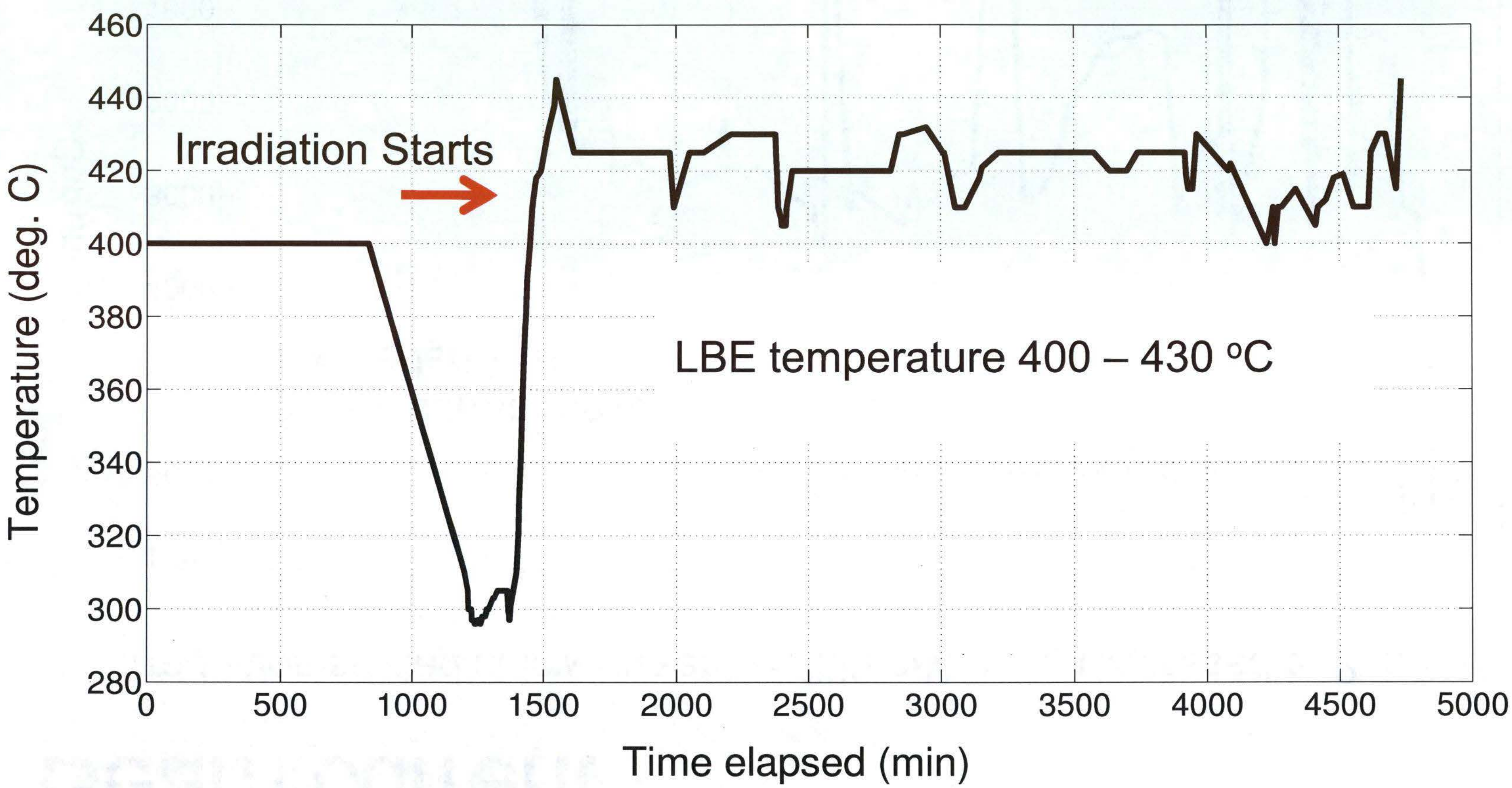
Sample temperature	450	°C
LBE (bulk) temperature	420	°C
Particle energy	5.50	MeV
Particle current	2.0	μA
Beam spot-size	3x3	mm
LBE oxygen content	300	ppm
Cumulative irradiation time	58	h
Cumulative LBE-melt contact time	80	h
Bulk sample DPA	3.8	dpa
Maximum sample DPA	22.1	dpa

Camera + scintillator system proved vital for beam position and size calibration

DPA profile in the sample

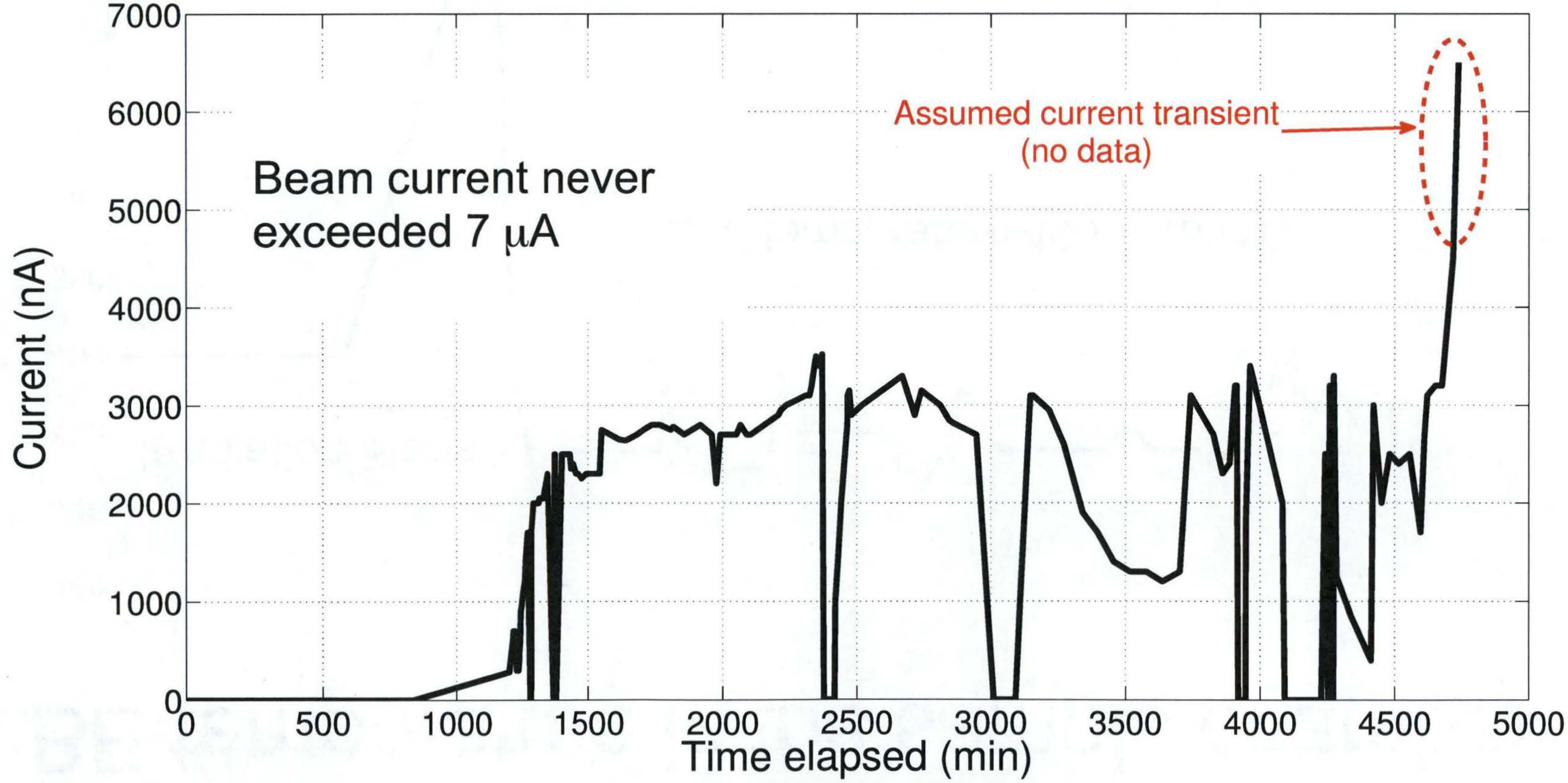


LBE temperature in the sample chamber



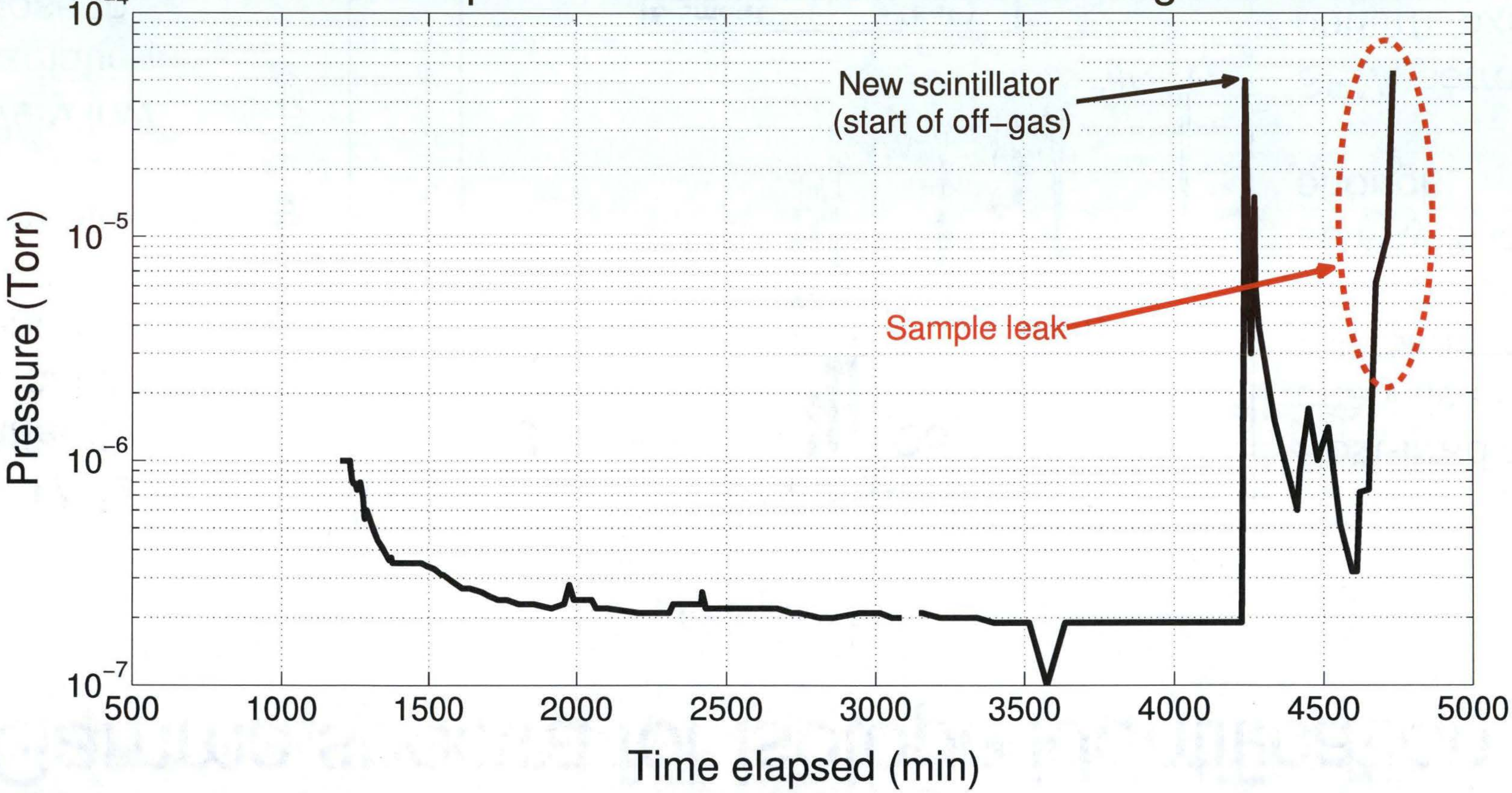
Beam current

Irradiation started at low current (~ 200 nA) and progressed to 2-3.5 μA



Pressure spike activated automatic stop

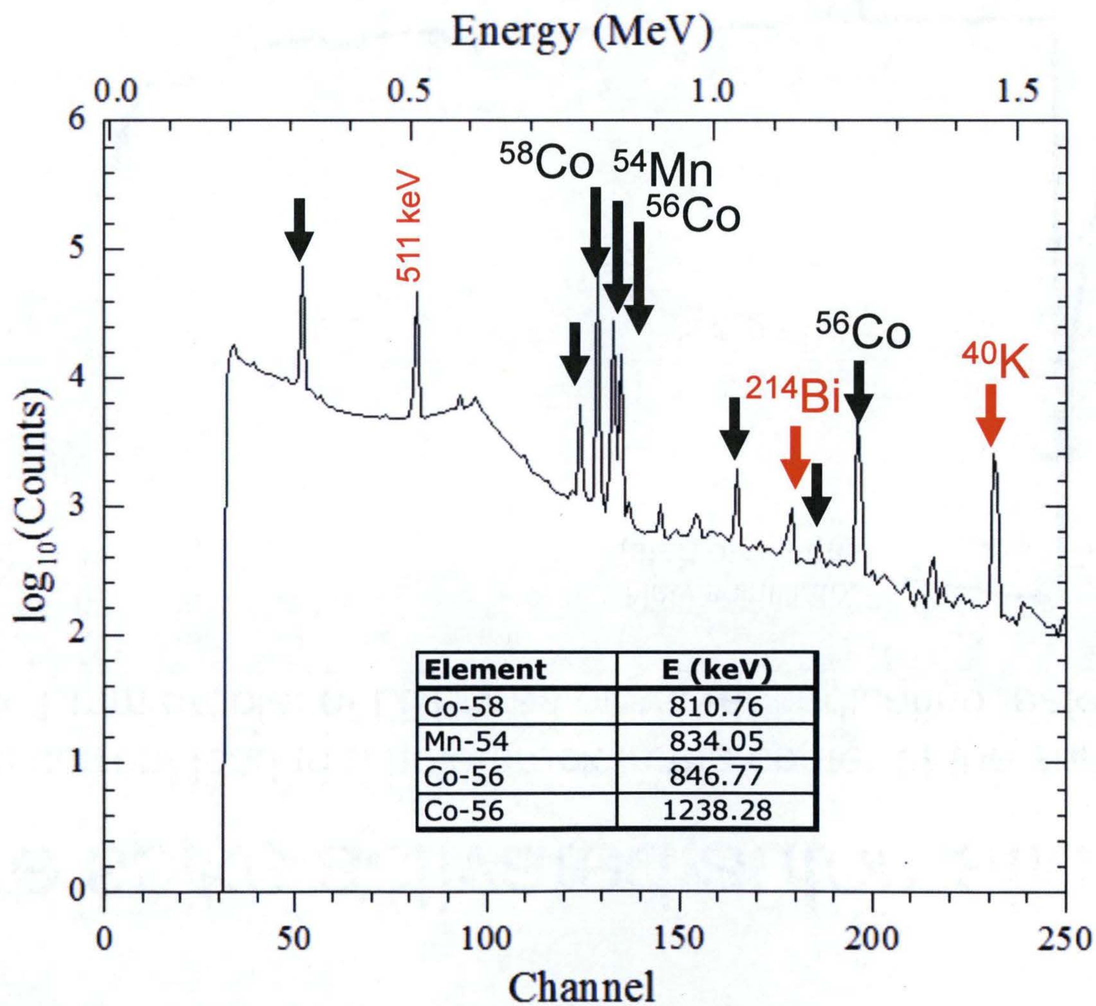
High beam current lead to a hole/crack in the center of the sample
A small 1 x 1 mm droplet of LBE was observed indicating leak location



Gamma spectra for isotope identification

~ 17 days after the irradiation ended a few peaks remain

Very low radiation dose in contact with the sample
< 7 mrem/h
< 0.3 μCi



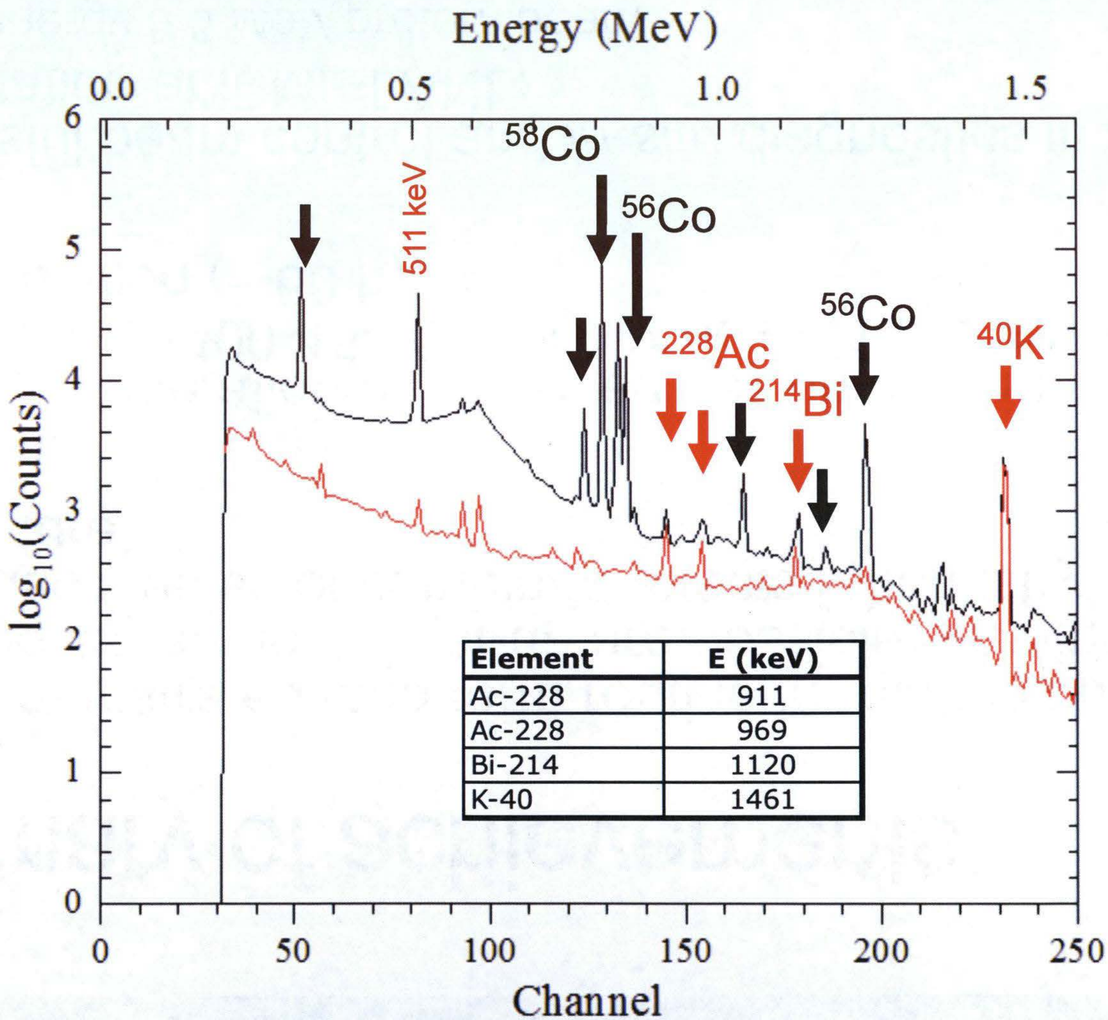
Element	E (keV)
Co-58	810.76
Mn-54	834.05
Co-56	846.77
Co-56	1238.28

Post-irradiation analysis (PIE) will take place once specimen activity is low enough

SEM, corrosion pattern, oxide layer thickness, etc.

Comparison between ICE2 and background gamma spectra

Background spectrum (red line) contains peaks from radiation emitted by naturally occurring radionuclides



Element	E (keV)
Ac-228	911
Ac-228	969
Bi-214	1120
K-40	1461

NEXT STEPS
Post-irradiation analysis (PIE):

Once specimen activity is low enough SEM, corrosion pattern, oxide layer thickness analysis will follow

Summary of achievements

- ICE2 demonstrated long term routine irradiations using the operating experimental set-up are possible allowing for systematic studies of combined effects (chemistry, dose, and temperature)

- Successful operation of improved design allowing for higher temperatures (400-450 C), higher dose (1.5 dpa), and long term irradiation (~ 60 h)

- Successful beam control and *in-situ* diagnostics in a dedicated beam station at IBML-LANL:
  - High energy 5.5 MeV proton beam
  - High beam current 0.3 μAmp
  - Successful test of the safety system installed on the accelerator beamline (fast response of gate valve that activates in accident scenarios)

Next steps

- ICE 3 Opportunity and Challenges
  - Isothermal LBE closed loop system
  - Experiments in reducing and oxidizing environments
  - Different materials (F/M – ODS steels, coated steels, zircalloy)
  - Tensile experiments, irradiation creep

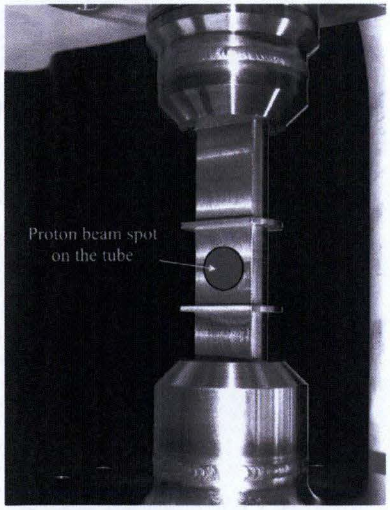
- Atomistic simulation of LBE/FeCr alloy interaction
  - First principles studies of Fe-Cr-Pb-Bi system
  - Pb-Bi interaction with FeCr alloys and formed oxides (Fe_3O_4 and $FeCr_2O_4$)
  - Effects of Cr redistribution in the material

Thank you!

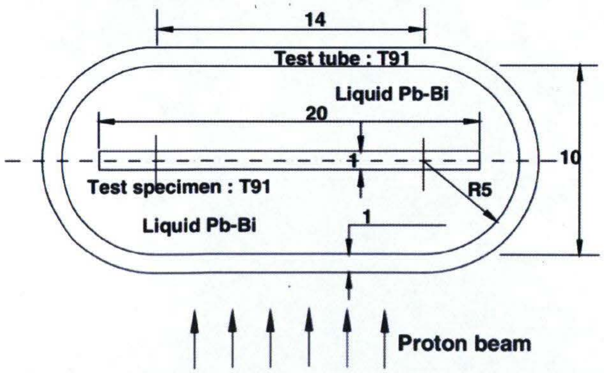
BACKUP SLIDES

Irradiation/Corrosion Synergistic Effects – scarce experimental data

- LiSoR : Liquid Solid metal Reaction irradiation facility at PSI.
- Candidate material T91
- Flowing LBE (flow rate = 0.8 m/s)
- Irradiation dose 0.75 dpa (70 MeV proton beam, 16 mA, 30 days)
- T = 380°C



Horizontal cut through the test tube and the test specimen in LiSoR



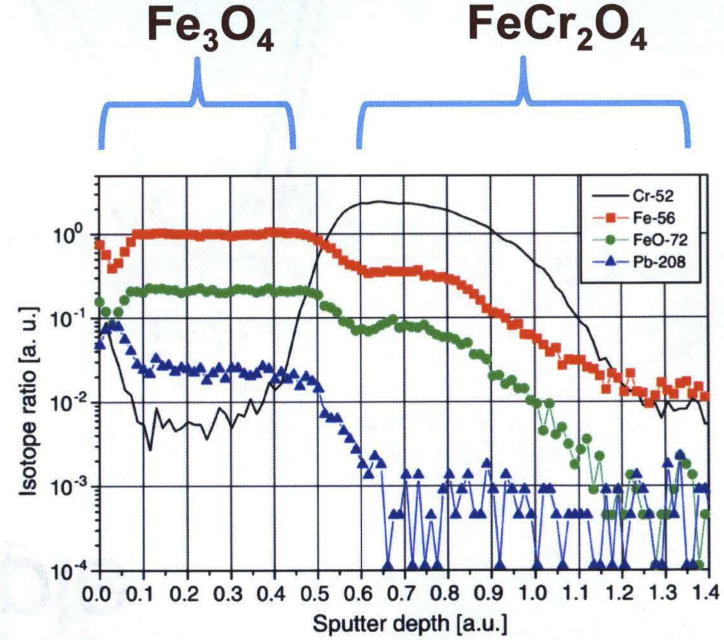
LiSoR loop (PSI)

T. Kirchner et al., JNM 318 (2003) 70

LiSoR – No irradiation effects found at 380°C

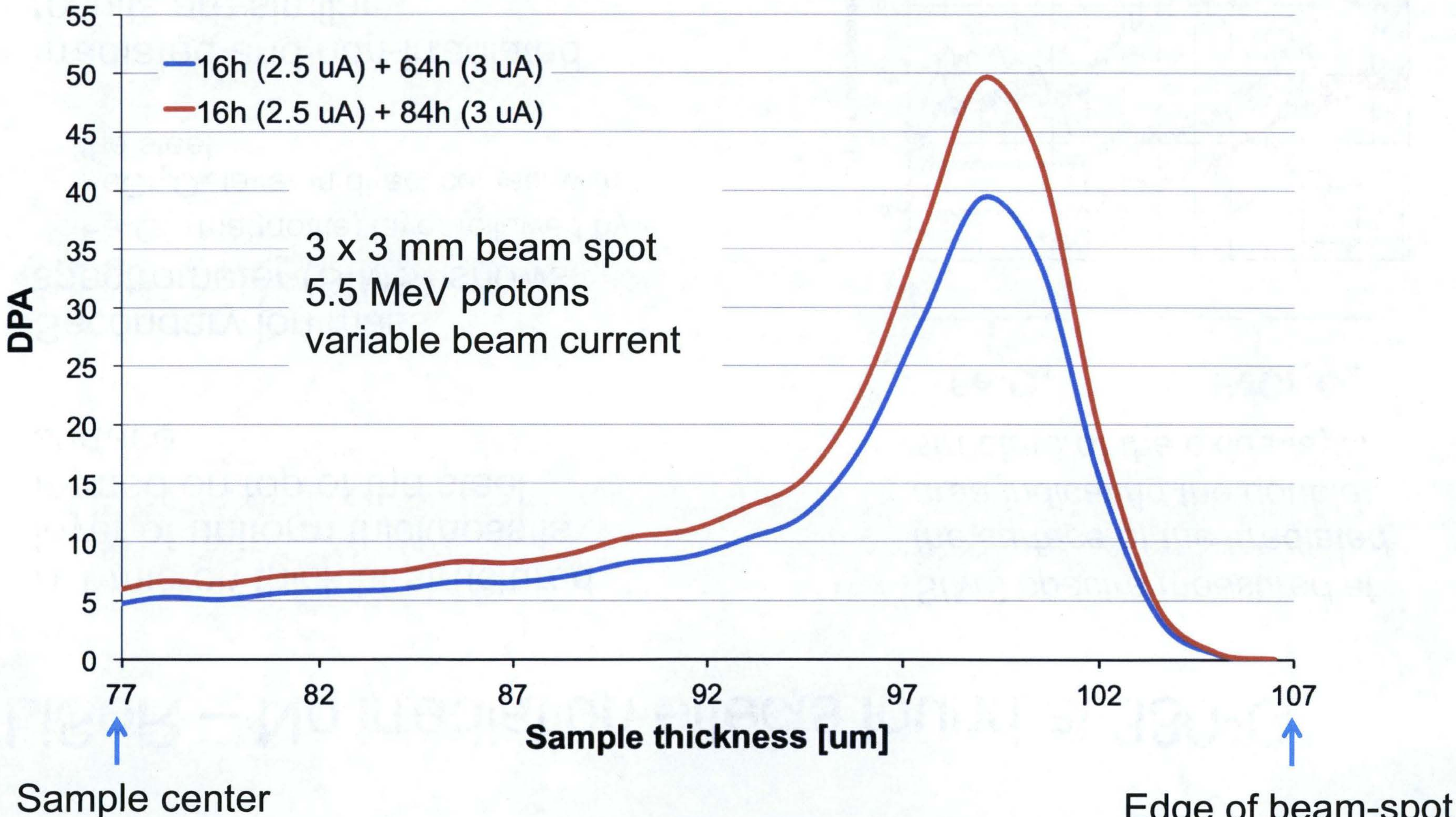
- A 1 micron thick bi-structured layer of uniform thickness is formed on top of the steel surface
- Secondary ion mass spectrometer (SIMS) shows :
  - Fe_3O_4 (magnetite) layer followed by
  - $FeCr_2O_4$ layer in direct contact with the steel
- Irradiated and non-irradiated results are similar
- Higher temperature needed to see the effect of irradiation

SIMS spectra measured at the surface of the irradiated area indicating the double structure of the oxide layer

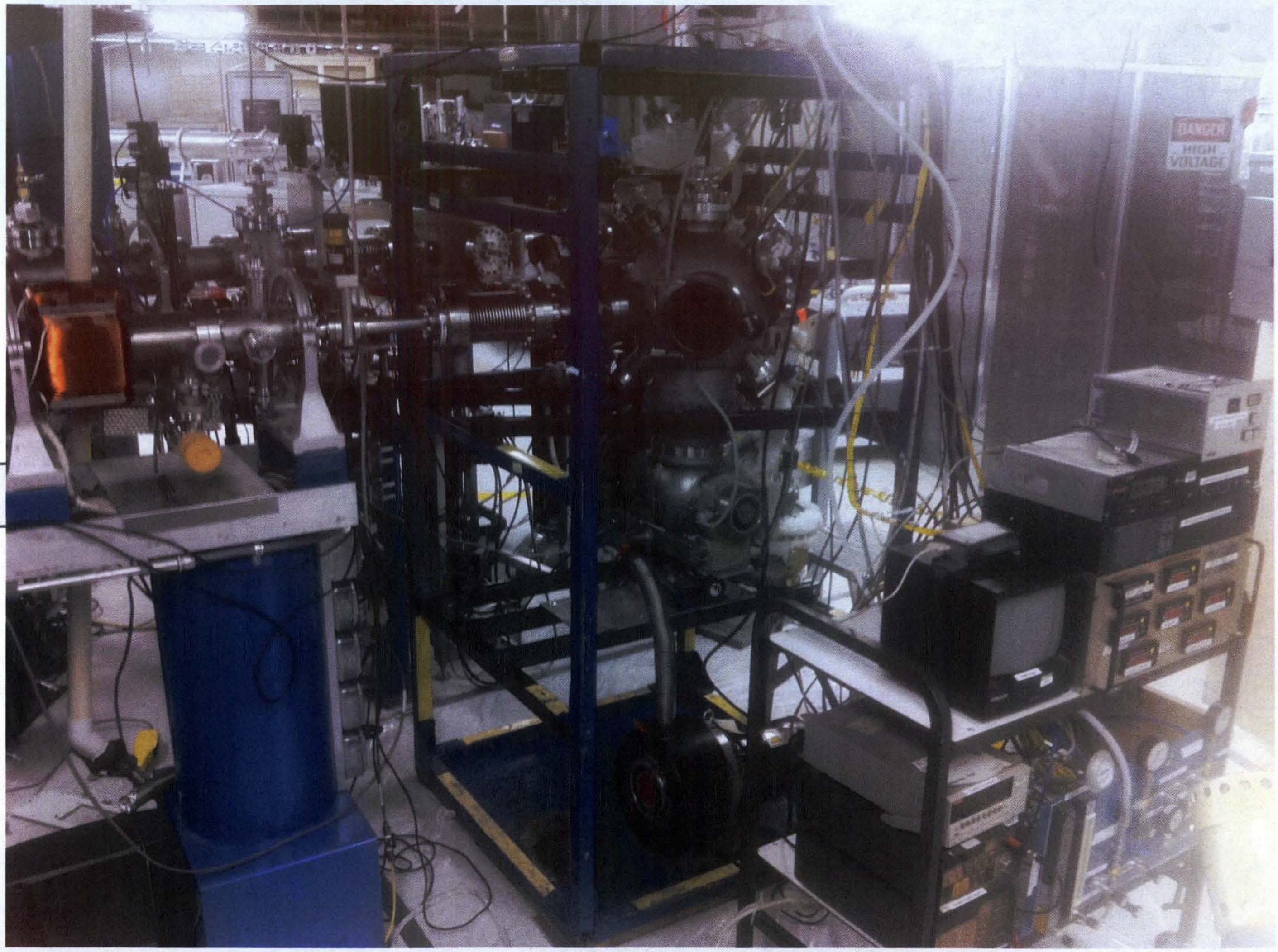


H. Glasbrenner et al., JNM 367–370 (2007) 1590

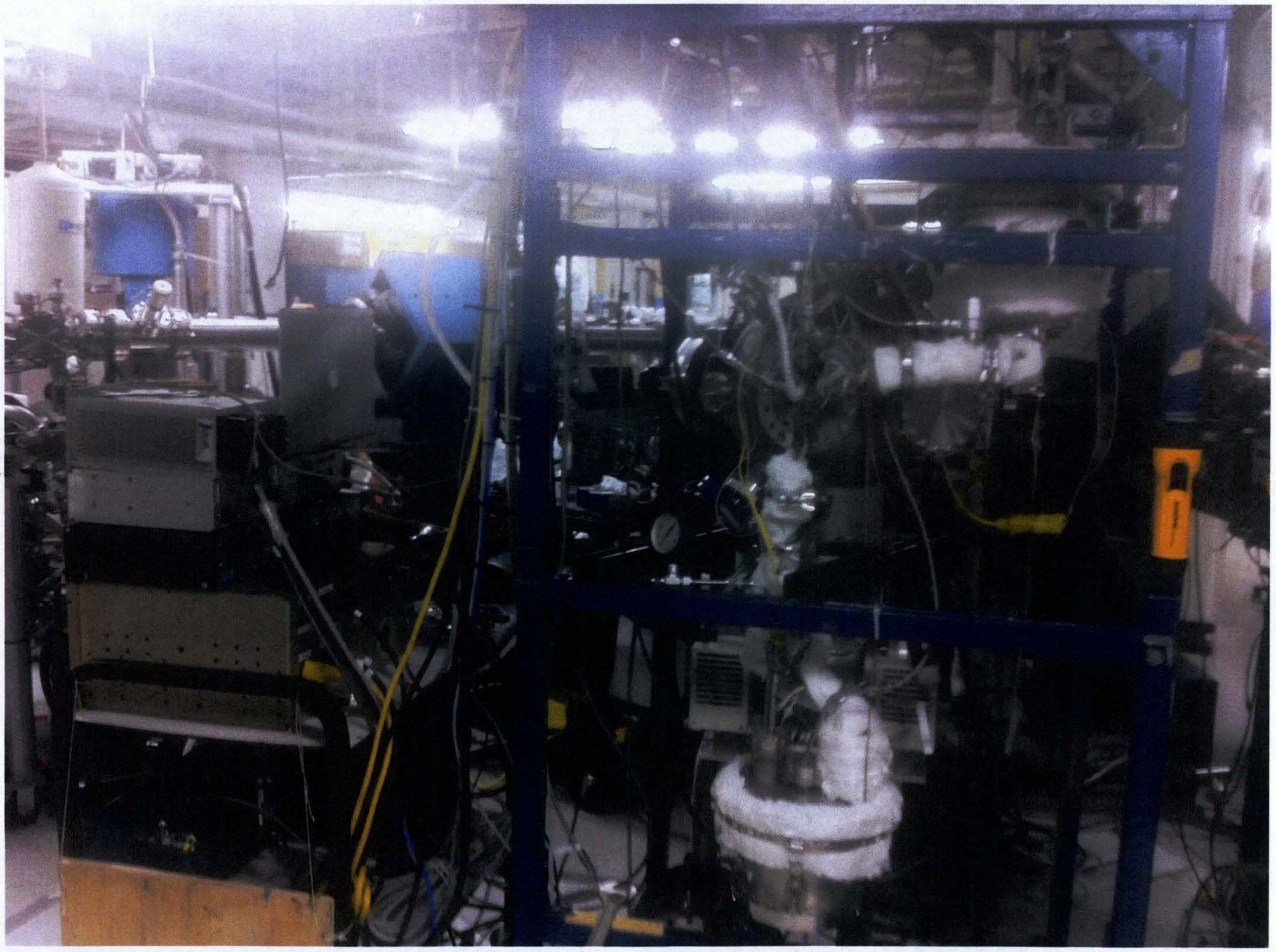
DPA profile in the sample



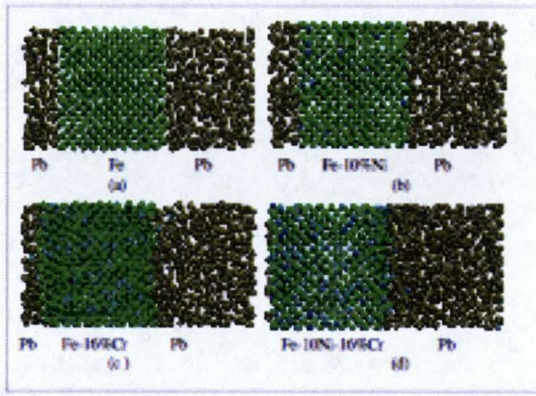
ICE2 station (View from side)



ICE2 station (View from back)



ICE2 station (Pressure system)


Pb
Fe
Pb
(a)
Pb
Fe-10%Ni
Pb
(b)
Pb
Fe-10%Cr
Pb
(c)
Fe-10Ni-10%Cr
Pb
(d)