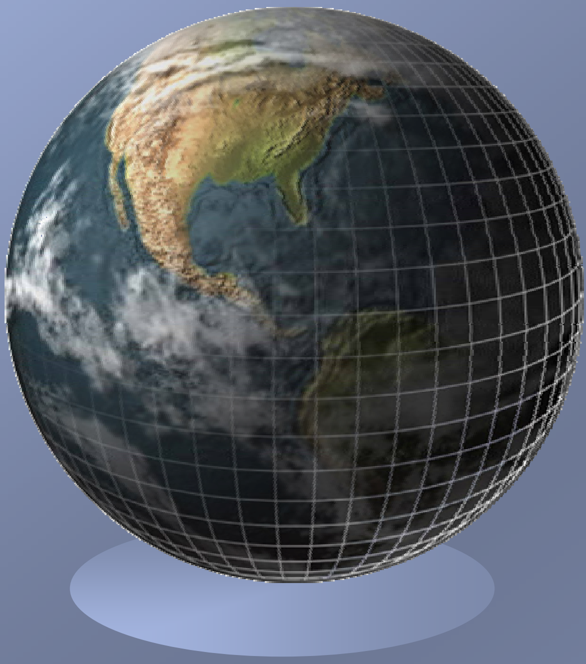
Candidate Materials and Coolant Technology for Lead-Alloy Cooled Nuclear Systems



-Metallic Alloys, Ceramics and Composites

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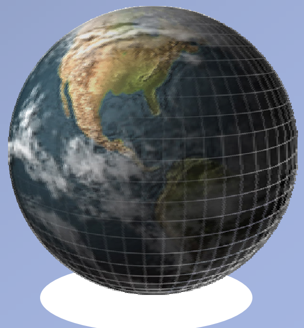
GEN IV Nuclear Energy Systems

AFCI

Outline

Three Broad Classes of Candidate Materials and Corresponding Coolant Technologies by Upper Operating Temperatures

- Class (I): 550-600^{o}C, Fe-Cr-Si steels with oxygen controlled LBE or Pb
- Class (II): 600-700^{o}C, improved (functionally graded) or ODS steels with oxygen controlled Pb
- Class (III): 700-1000^{o}C, refractory metals and alloys, ceramics and composites in oxygen free Pb

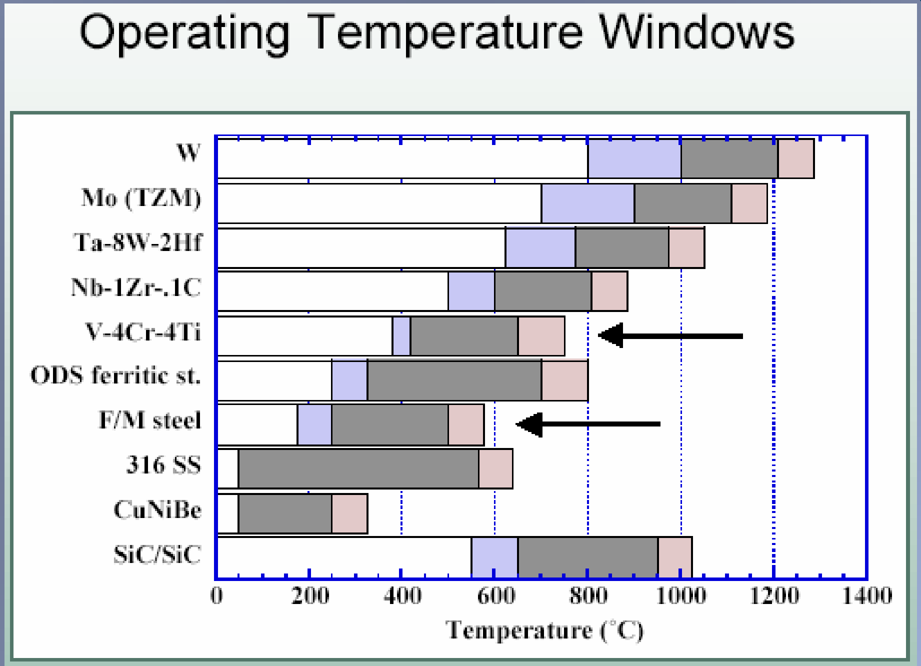


Challenges

- Compatibility, corrosion and oxidation are key obstacles for use of steels in LBE/Pb
- Loss of strength above 600^{o}C is also limiting for steels
- New classes of high-temperature materials (ceramics and composites) are limited by factors other than compatibility

Temperature Ranges of Candidate Materials in Nuclear Systems

- Lower limit determined by radiation embrittlement and margin to prevent coolant freezing
- Upper limit determined by thermal creep and radiation effects, but in many cases by coolant compatibility and corrosion
- Oxidation can also be limiting



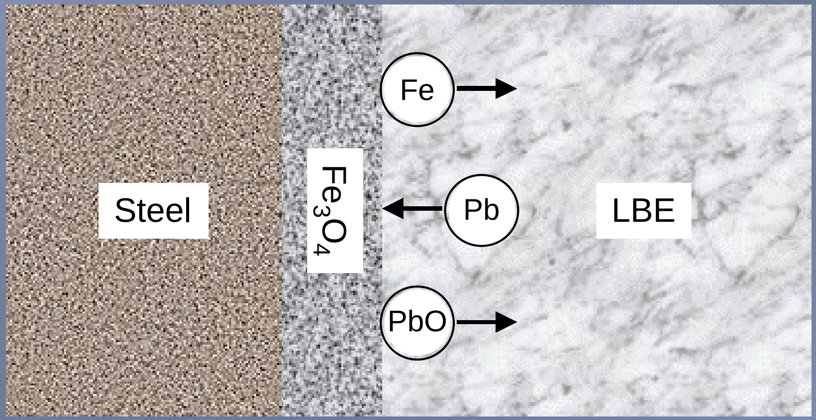
S.J. Zinkle and N.M. Ghoniem (2000)

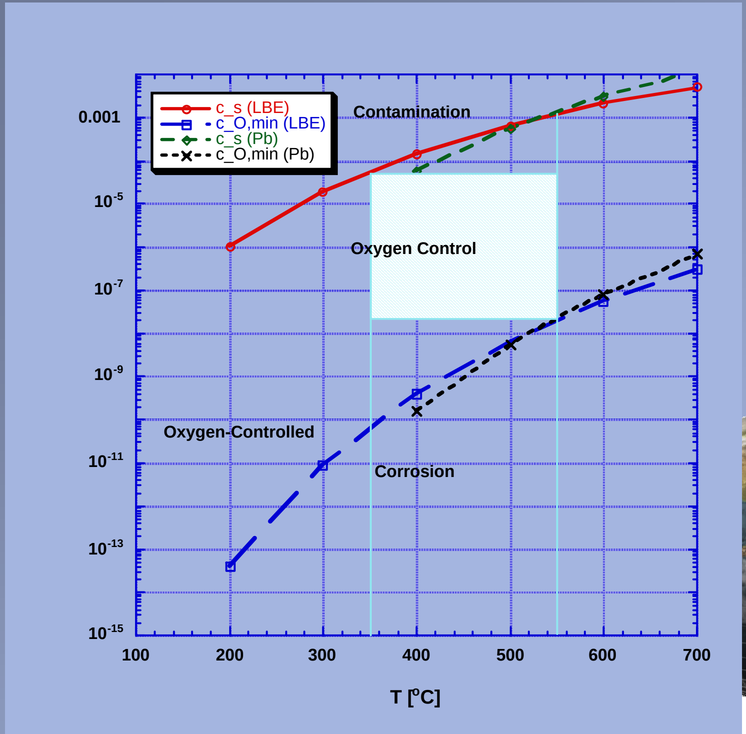
Class (I): Steels with Oxygen Control in LBE/Pb

- Baseline choice derived from Russian submarine LBE reactor experience, then BREST (Pb-cooled)
- Significant international development in support of ADS and Gen IV LFR
- Materials and coolant technology (oxygen control) more mature for LBE
- For Pb, the narrower temperature window and less developed coolant technology require more development - however, Pb is clearly the choice for higher temperature, higher performance, large-scale deployment systems

Oxygen Control is Key to Protect Steels with Oxides in LBE/Pb

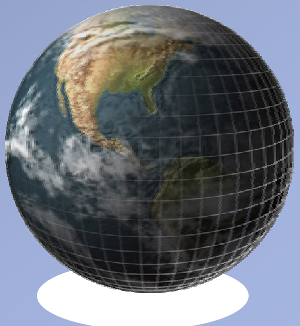
- Fe, Cr, and esp. Ni have substantial solubility in Pb and Bi
- It's possible to adjust oxygen potential in LBE/Pb to form in-situ "self-healing" oxides on steels for protection
- Steels with good oxidation resistance show good performance in corrosion testing in oxygen controlled LBE/Pb





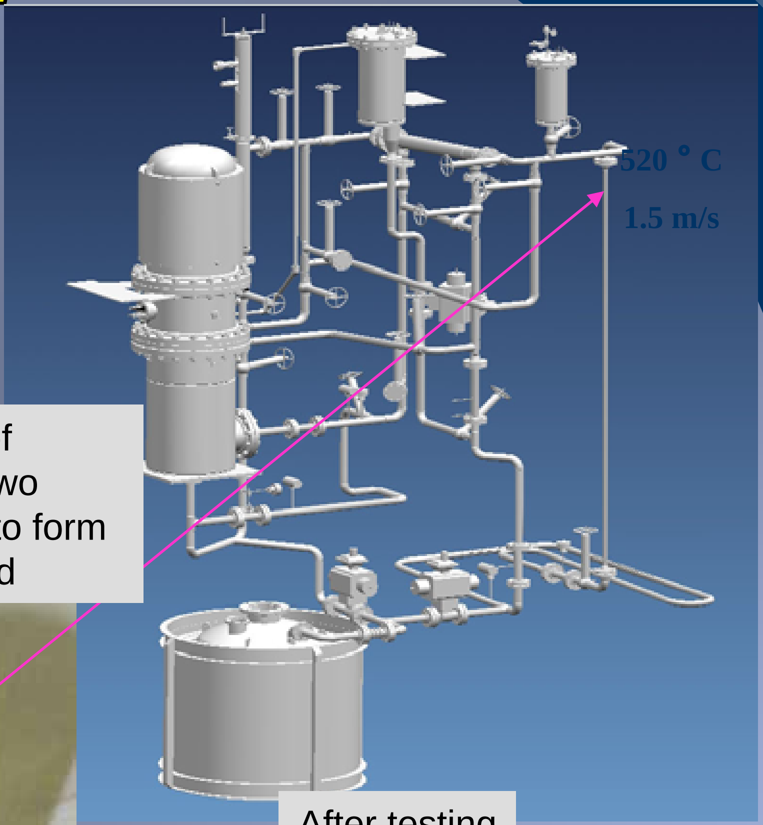
International R&D

- Russian BREST and SVBR programs
- EU EUROTRANS (DEMETRA), Japan J-PARC, TITech COE-INES, US AFCI/Gen IV LFR, S. Korea PEACER/HYPER, …
- Close to 40 LBE/Pb test loops and devices in OECD countries, in addition to Russian’s facilities
- Many organizations begin to master oxygen control and other aspect of coolant technology
- Corrosion testing of large selection of materials narrowed selections and conditions
- Alternative protection methods being developed



LANL Test Program: DELTA Loop

1000 hrs at 450^{o}C, and 400 hrs at 520^{o}C.
Over 20 materials.
~1.5 m/s LBE flow speed



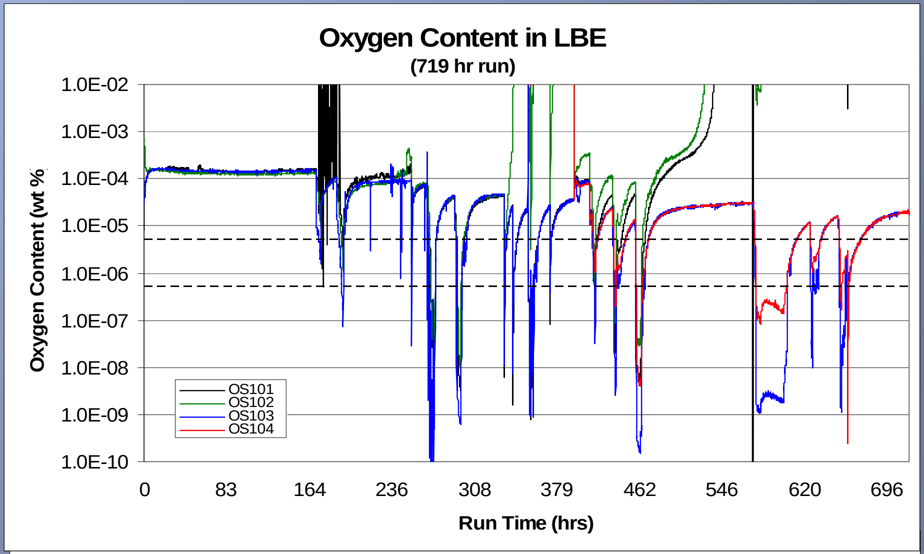
Corrosion test specimens

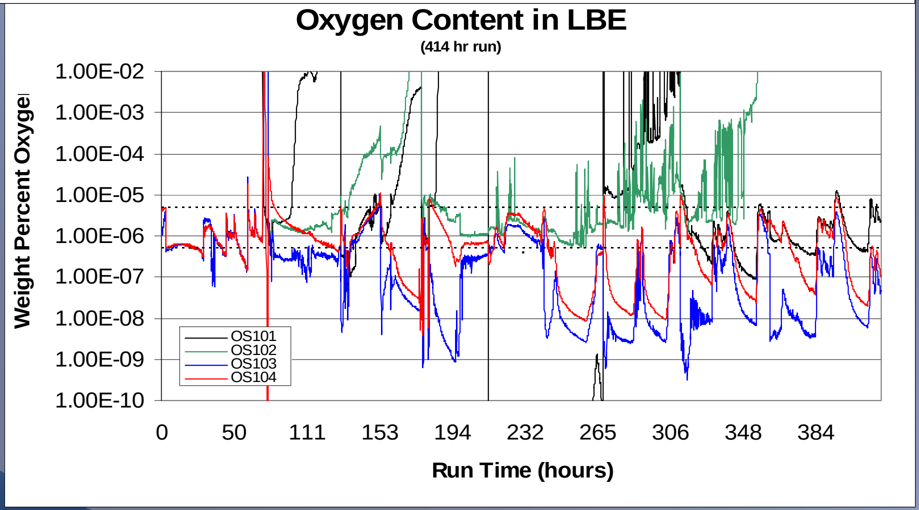
Two batches of samples and two batches used to form flow assembled

Sample holders (slotted channels)

After testing

Oxygen Measurement & Adjustment Achieved in DELTA - Improvement in Control Needed



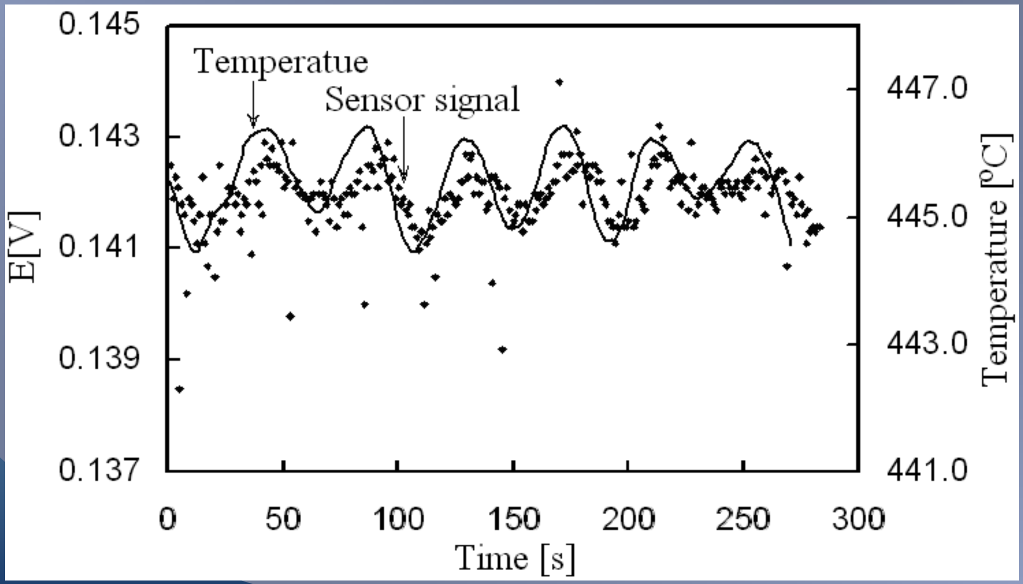


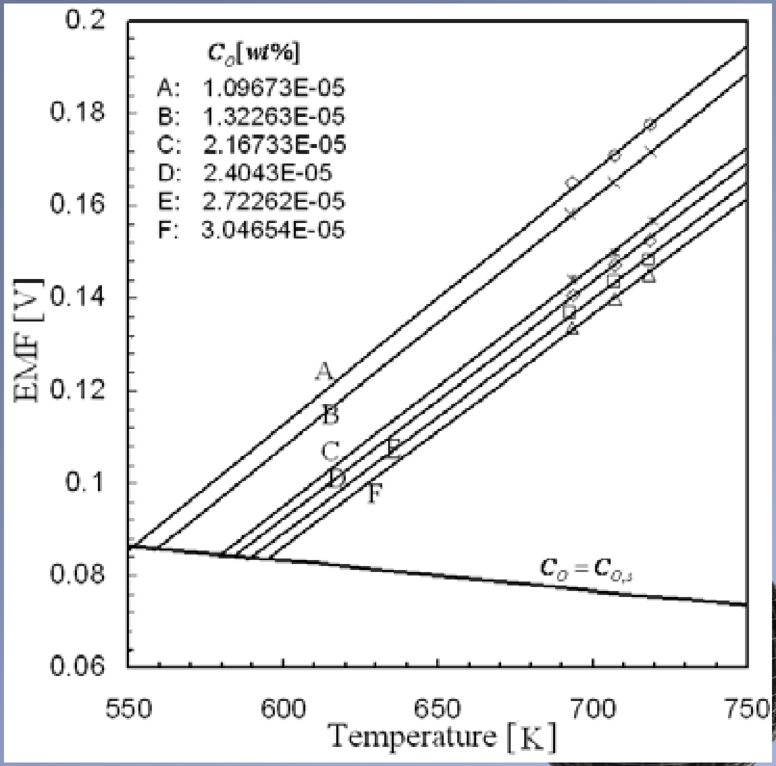
- An improvement can be observed in oxygen control during the 400 hour run
- Oxygen sensors did not track one another well during the 400 hour test: Bi reference corrodes tantalum and SST signal wires at high operating temperatures
- Oxygen sensor failures were frequent at high temp; inaccurate readings complicate oxygen control
- Oxygen adjustments were manual, which made it difficult to maintain oxygen control 24 hours a day

Oxygen Sensors Performed Well Below 500^oC - Improvement Needed for Higher T

- The oxygen sensors signals were good when functioning below 500^{o}C
- Oxygen concentration in LBE is uniform but varied in time due to adjustment

(Solid lines are calculated based on Nernst theory)



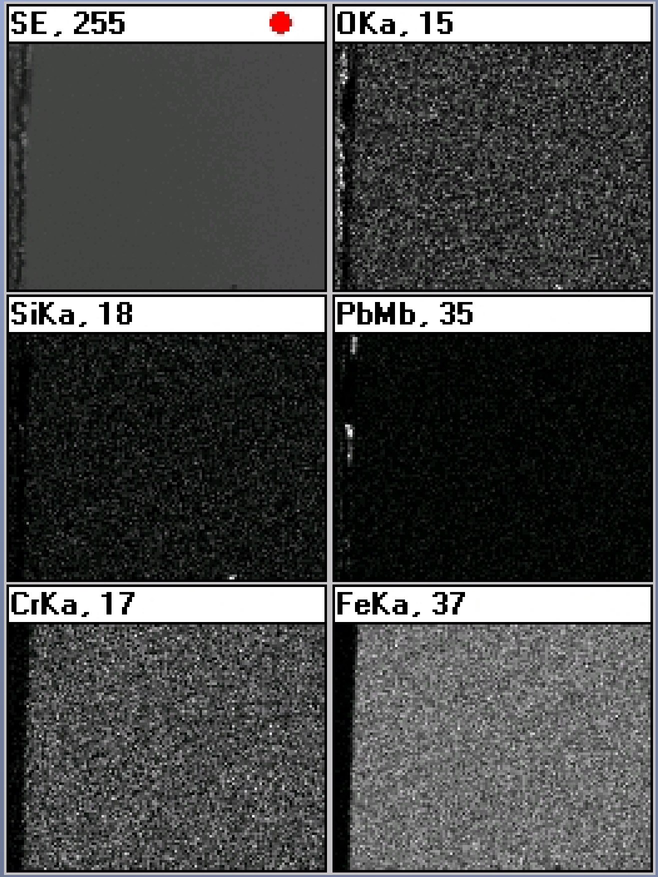


Analysis of Specimens Tested in DELTA for 1000-hrs

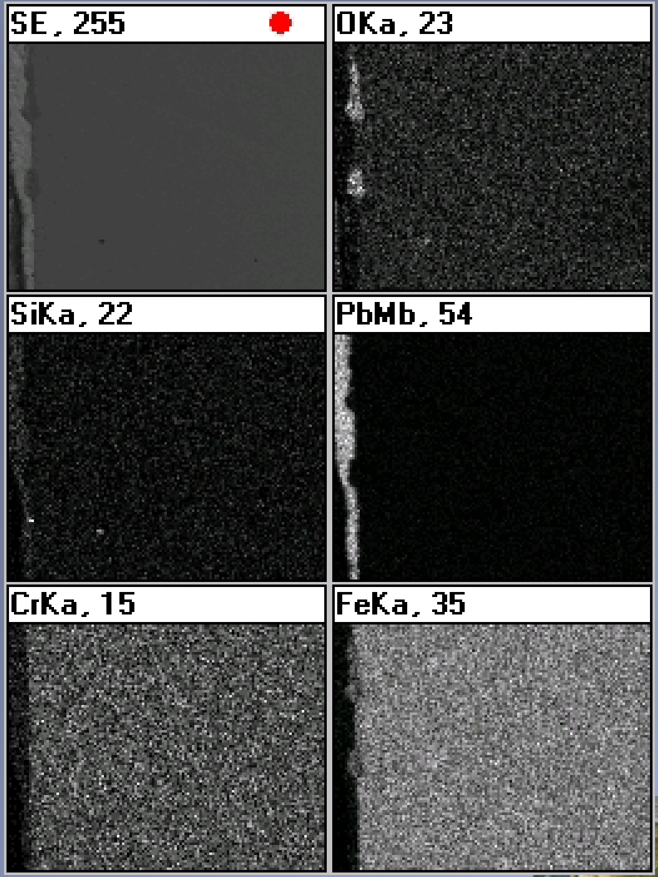
- Materials tested: 20+
- Three time intervals (333, 667, 1000 hrs)
- Test temperature: ~ 450^{o}C
- LBE flow velocity: 1.5 m/s (?)
- Oxygen concentration: varied due to cleaning of excess oxides, target 10^{-6} wt% could be achieved but not maintained for extended periods

Material	Cr wt%	Si wt%	Ni wt%	C wt%	Mo wt%	Mn wt%
FeCr1	1	-	-	-	-	-
FeCr2	2,25	-	-	-	-	-
FeCr3	9	-	-	-	-	-
FeCr4	12	-	-	-	-	-
FeSiCr1	2,25	0,5	-	-	-	-
FeSiCr2	2,25	1,25	-	-	-	-
FeSiCr3	12	0,5	-	-	-	-
SiFe1	0,09	1,24	0,08	0,01	-	-
SiFe2	0,08	2,55	0,15	0,02	-	-
SiFe3	-	3,82	-	0,01	-	-
pure iron	-	-	-	-	-	-
T91	8,26	0,3	0,13	0,1	0,95	0,38
EP823	12	1,3	0,8	0,18	0,9	0,8
HT-9	11,5	0,4	0,5	-	-	0,6
316L	17,3	0,35	12,1	0,02	2,31	1,8

Fe-12Cr-0.5Si - Protected by Thin Oxide (0.5wt%Si Enhanced Oxidation Protection)

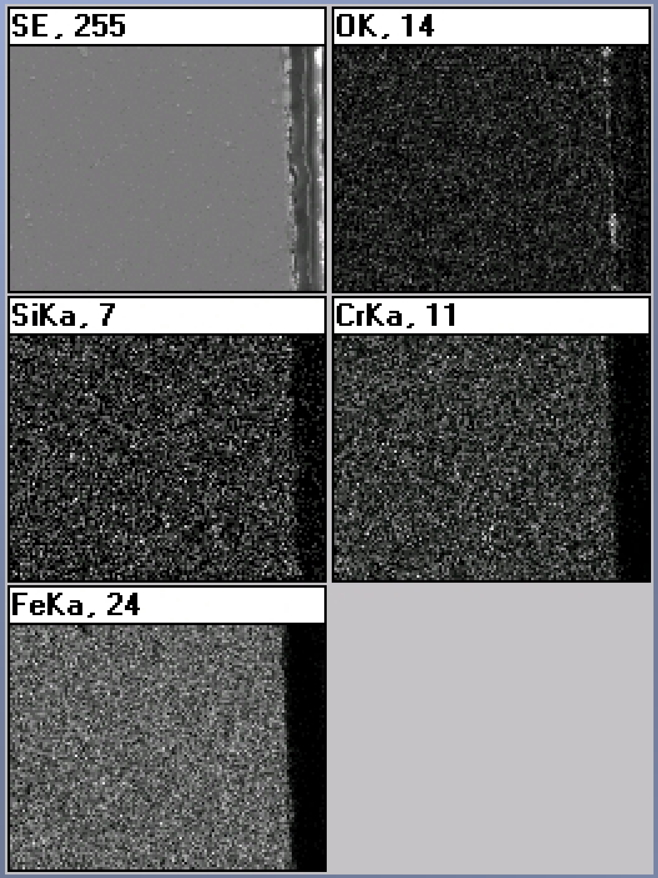


Polish Side

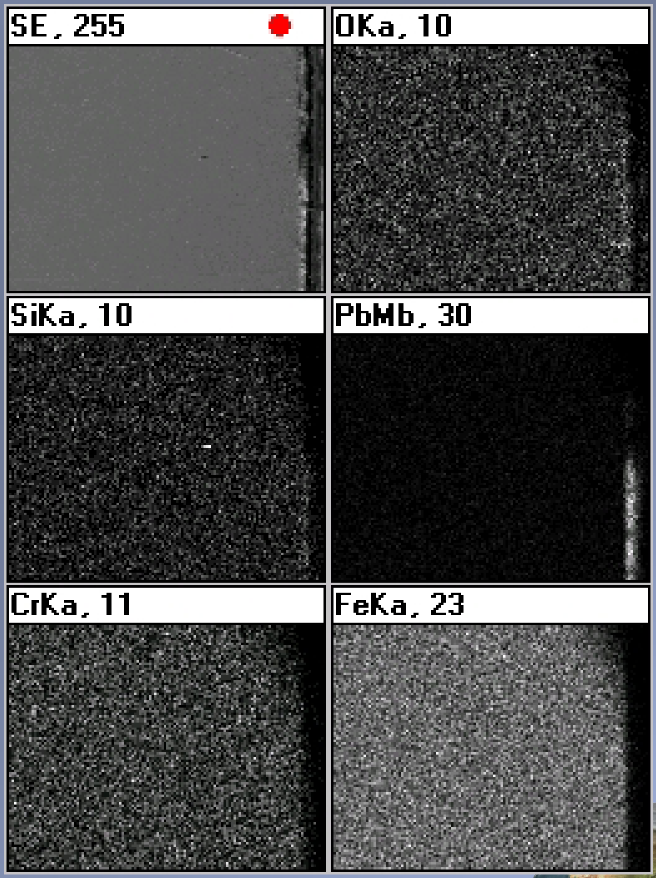


Unpolished Corner

EP823 Well Protected by Thin Oxide

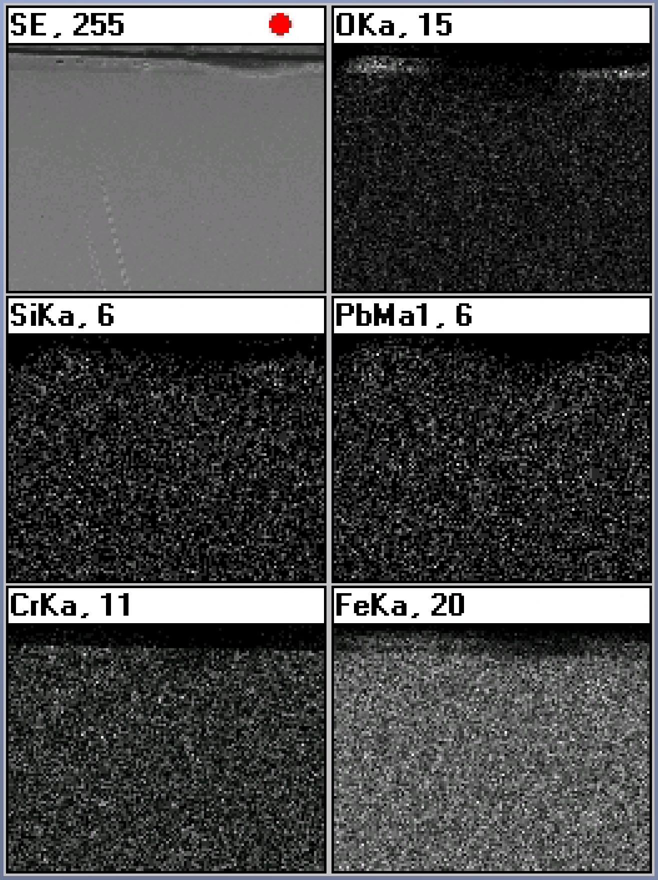


EP823 (IPPE)

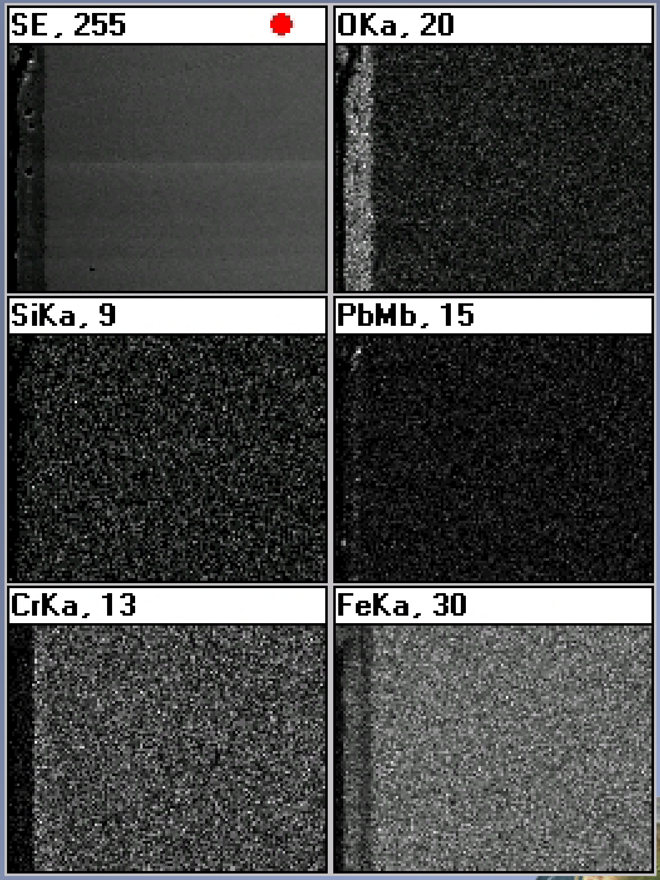


EP823 (Timken)

HT-9 - Protected by Thick Duplex Oxide (May not be Suitable for Long-Term Use)



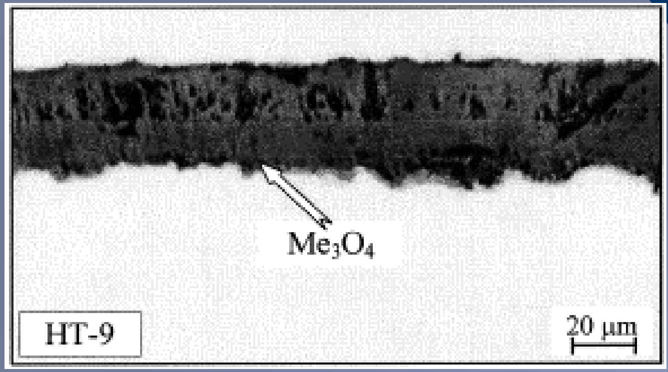
HT-9 (ANL)



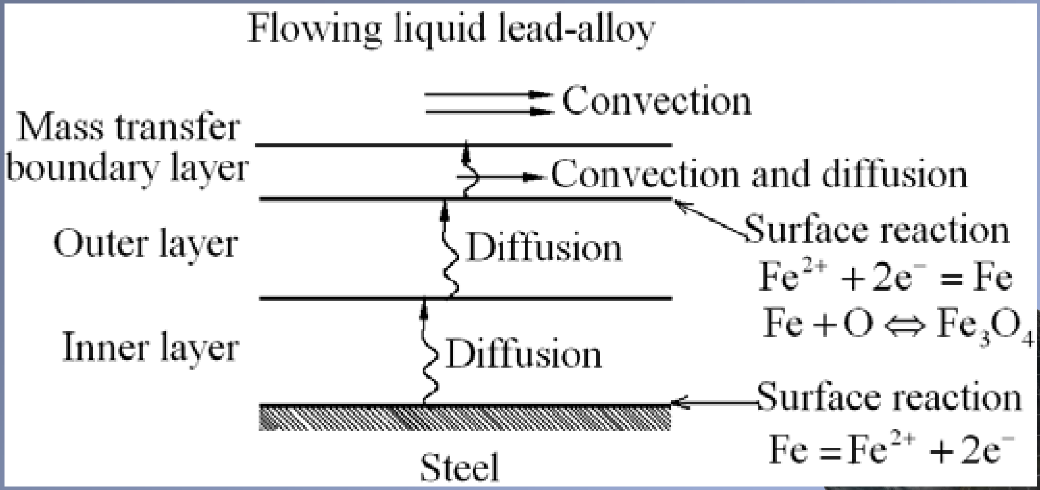
HT-9 (Timken)

Modeling Oxidation/Corrosion Based on First Principles and Experimental Findings

- Oxide scale:
  experimentally observed structures

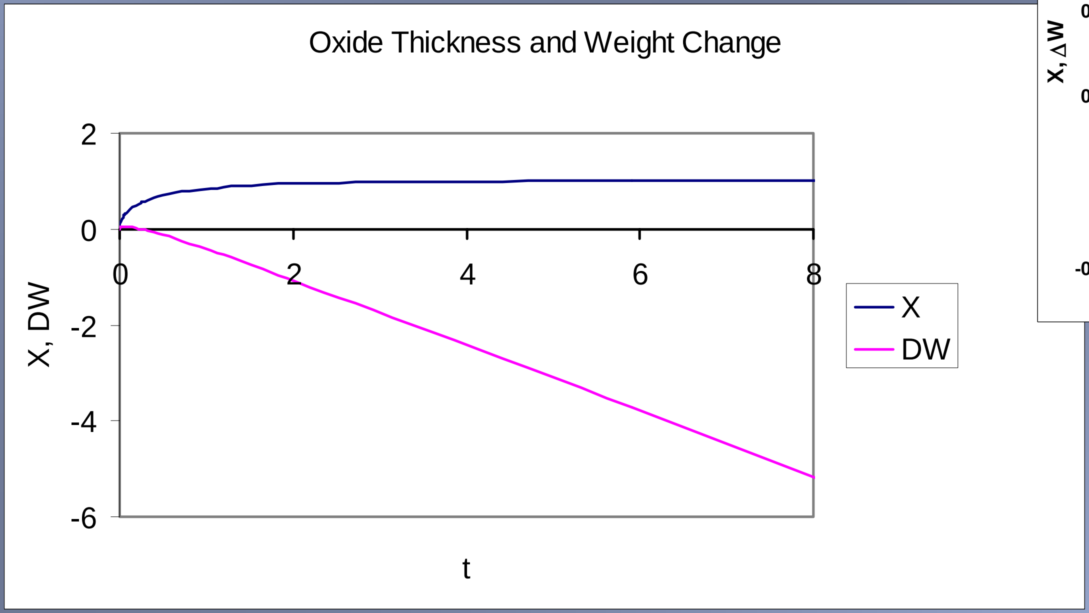


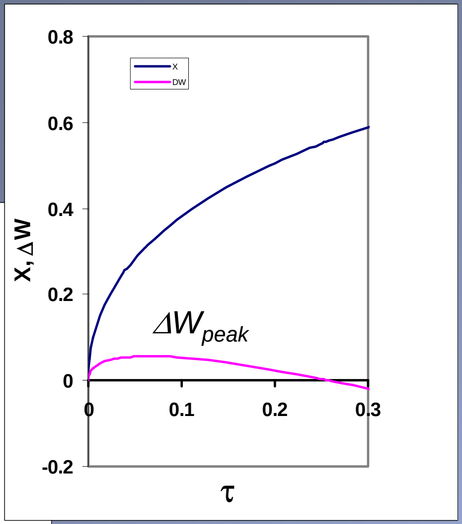
- Mass transfer in liquid metals:
  turbulence model

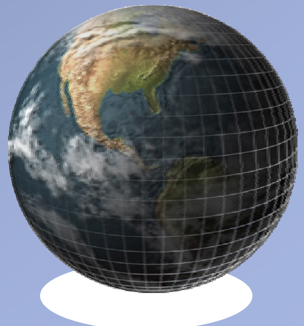


Different Growth/Destruction Regimes Can Be Categorized with a Universal Solution

- Oxide grows by parabolic law initially
- Weight gain due to oxidation peaks early
- Oxide thickness stabilizes in long-term*
- Weight loss becomes linear in long-term*



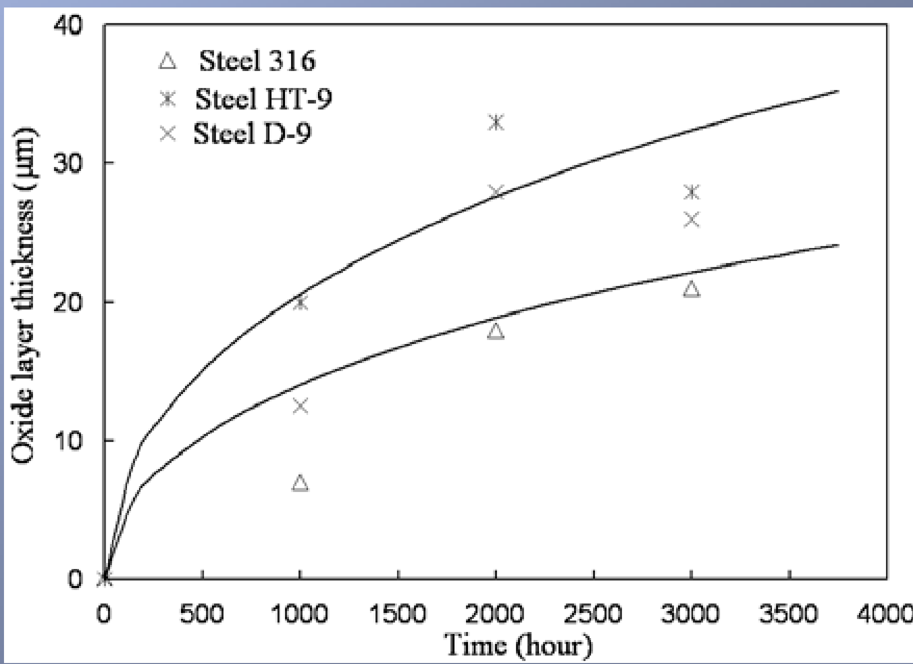


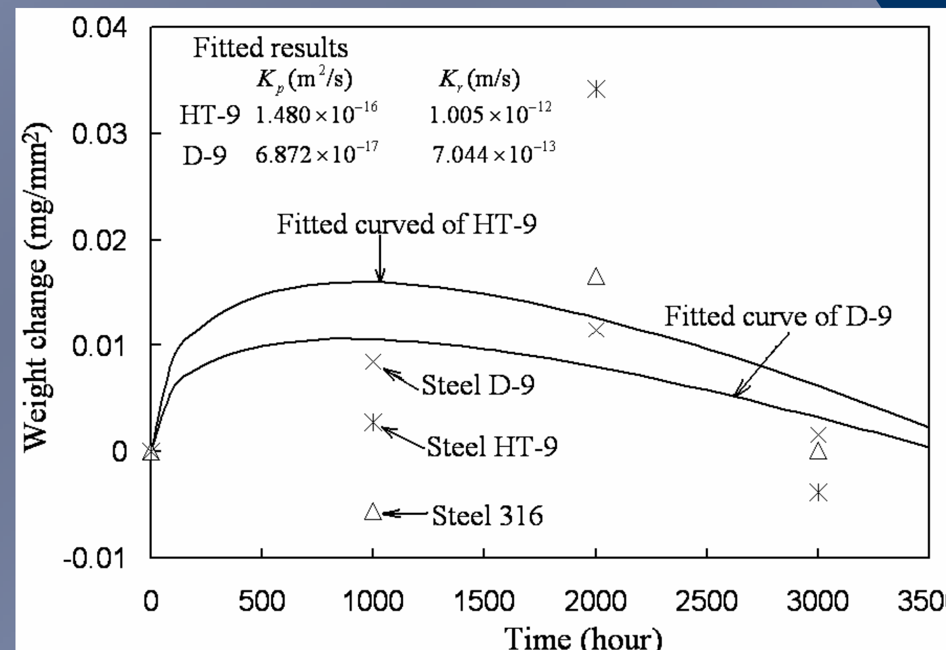


* Assuming oxide is stable (does not crack, spall, eroded or enter break-away oxidation)

The Kinetics Model Used to Obtain Rate Constants from Corrosion Test

Asymptotic oxide thickness:
HT-9: 74 μm, D-9: 49 μm.



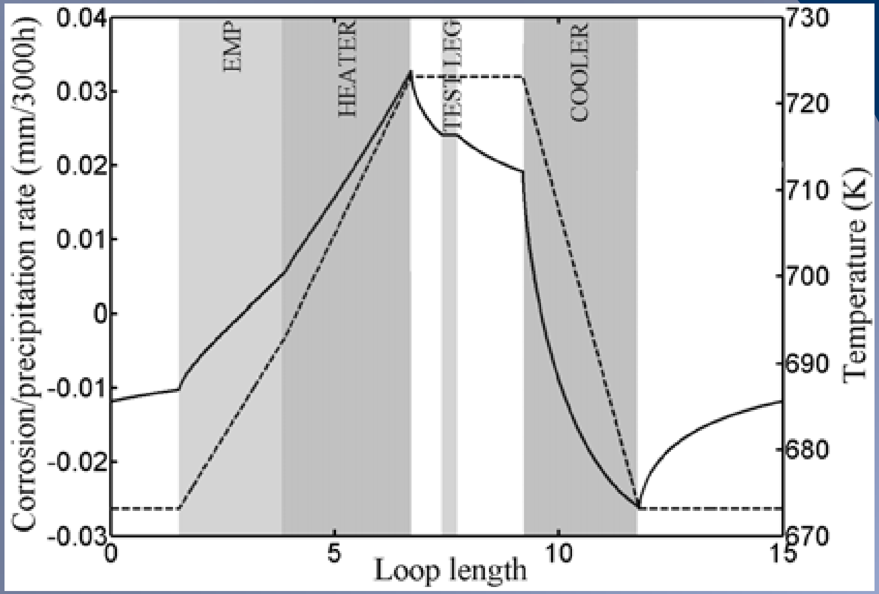


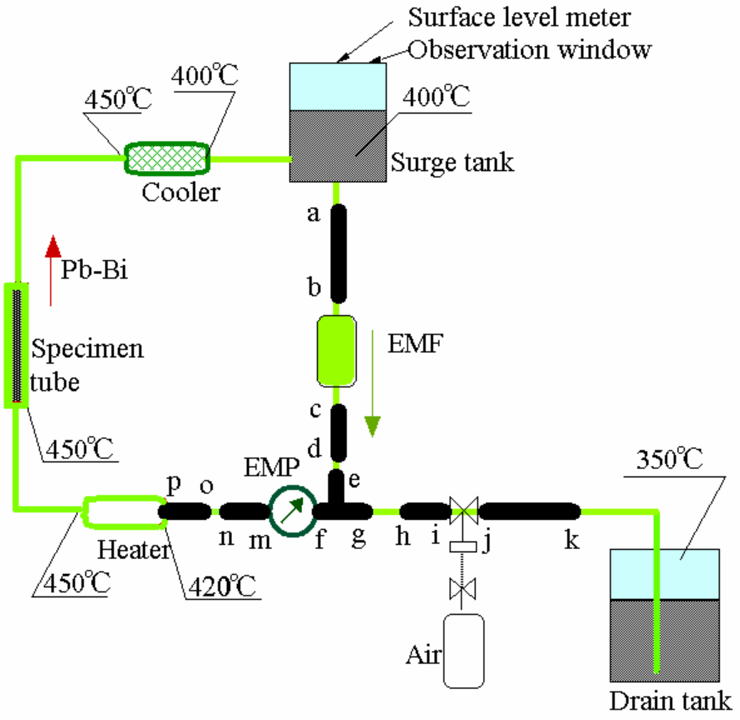
- Oxidation resistance appears to be positively related to long-term corrosion resistance
- Testing longer than 3000 hrs (6000 hrs or longer) at 500°C or higher needed for direct measurement of long-term corrosion resistance, but short-term testing (a few hundred hrs) may screen out materials with oxide resistance/stability problems
- HT-9 and D-9 are not well suited for long-term use in medium to high temperature lead-alloy systems
- Break-away oxidation not considered (worst case scenario)

Benchmarking of Corrosion Model against JLBL-1 (JAERI Lead-Bismuth Loop) Experiment

- Calculated corrosion/precipitation rate for iron (solid line) and the temperature profile (dashed line) for JLBL-1 loop.

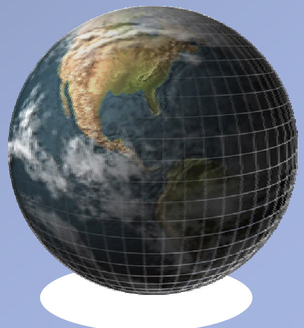
- Deposition zone (thick back line) JLBL-1 experiment. The corrosion rate is between 0.03-0.1 mm at the highest temperature leg.





International LBE/Pb Corrosion Test Results (mostly for 3000 hr or less)

- With oxygen control (~10^{-6} wt% in LBE)
  - 316 L -type austenitic steels, and T91, HT-9 type ferritic/martensitic steels can be protected up to ~550^{o}C
  - At ~600^{o}C, oxide cannot protect austenitic steels
  - Oxide on most F/M steels may grow too thick for long-term use at ~500^{o}C or higher
- Oxygen level < ~10^{-7} wt%
  - Austenitic and F/M steels may suffer dissolution attack even at ~400^{o}C
- Oxygen level < ~10^{-8} wt%
  - All steels appear to suffer dissolution corrosion (in addition, liquid metal embrittlement may occur at 400^{o}C or lower)



Alternative Corrosion Protection Methods and Coolant Technology

- Al-coating (GESA or interdiffusion) may protect steels up to 600-650^{o}C (oxygen controlled at ~10^{-6} wt%)
- Zr, Ti inhibitors, with Mg, added in LBE/Pb to form in-situ nitride/carbide on low alloy steels (oxygen free)

Class (II): Proper Concentrations of Cr and Si May Enhance Steel Corrosion Resistance

- Tests of Si-added EP823 show good resistance to corrosion and oxidation (but appears to suffer radiation embrittlement at lower temperatures)
- 9-12% Cr, 1-2.5% Si (higher Cr and Si may be detrimental in radiation environment) may be optimal and may allow for lower oxygen concentration (less oxidation)
- Combining radiation resistant steels with a corrosion resistant overlay (similar base compositions, with optimized Cr and Si, to avoid interface problems common in coatings) may increase the allowable temperature to 600-650^{o}C (then limited by loss of strength)

ODS Steels: Moving up the Temperature Limit to 650 – 700^{o}C

- Improved high temperature mechanical properties

ELSEVIER
Journal of Nuclear Materials 307–311 (2002) 749–757
journal of nuclear materials
www.elsevier.com/locate/jnucmat
Section 8. Dispersion-strengthened alloys

Perspective of ODS alloys application in nuclear environments

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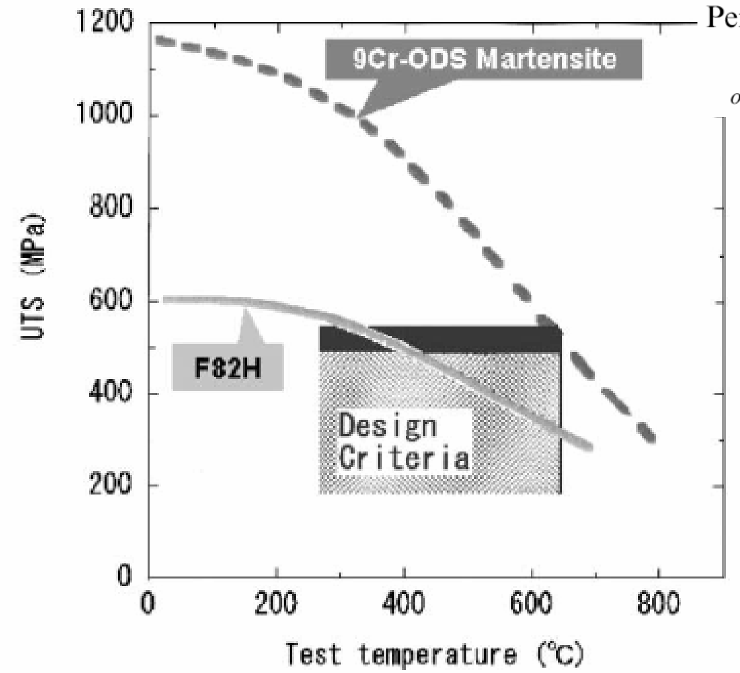
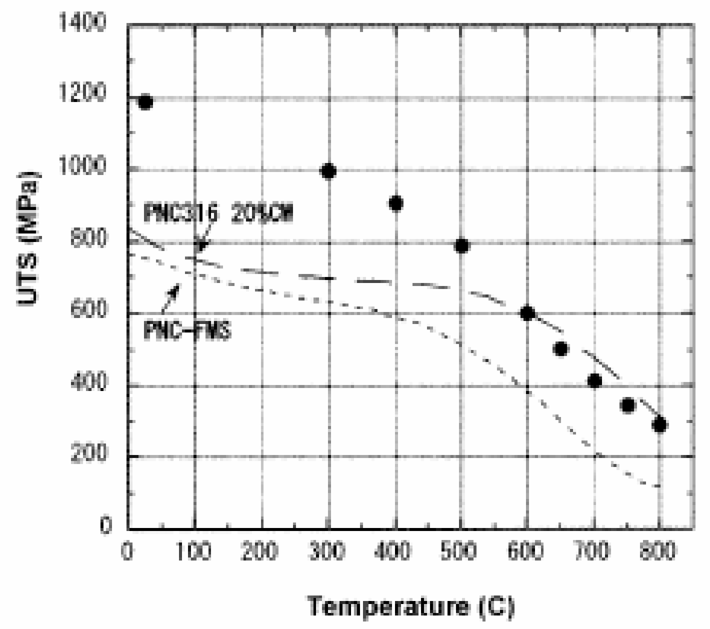


Fig. 8. Comparison of UTS in martensitic 9Cr-ODS steel cladding, F82H and tentative design criteria for fusion reactor materials.



In Oxygen-Controlled LBE/Pb, Corrosion Resistance ~ Oxidation Resistance

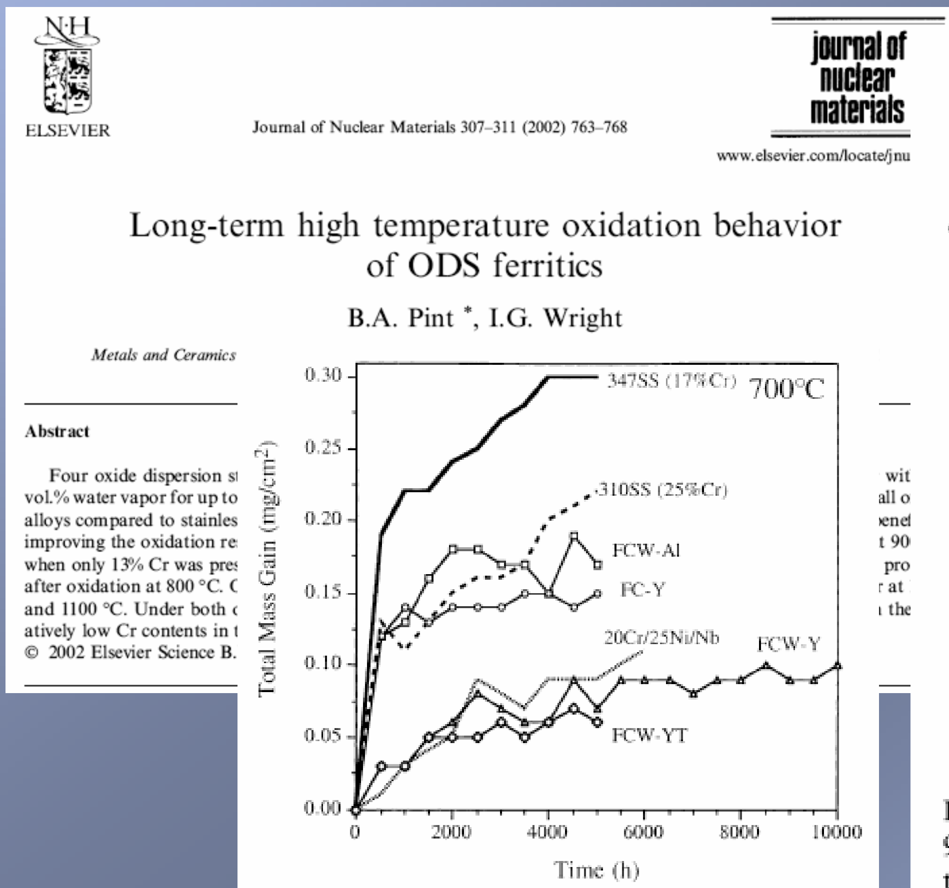


Fig. 1. Total mass gains measured during 500 h cycles in air at 700 °C for the ODS ferritic alloys and several reference alloys.

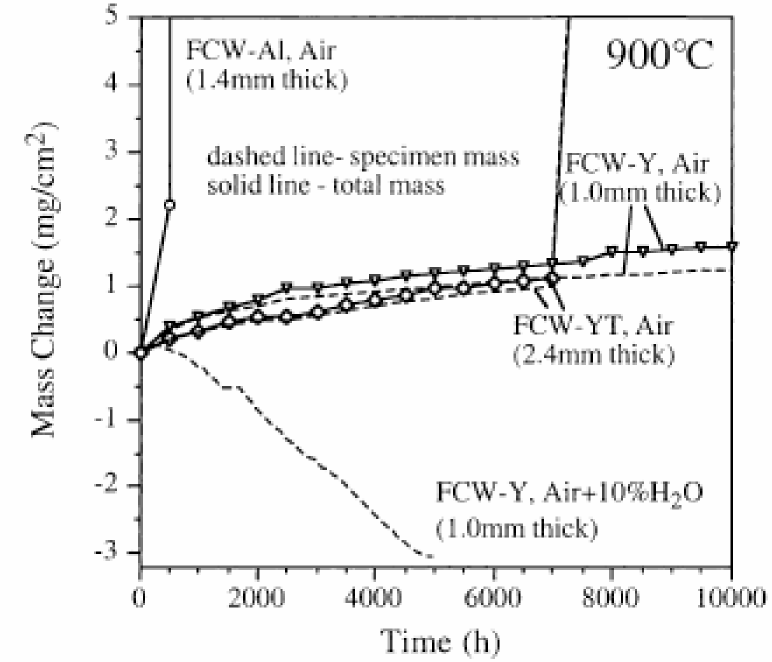


Fig. 3. Total (—) and specimen (---) mass gains measured at 900 °C in air and air with 10% water vapor. The specimen thickness is shown for each. The addition of water vapor to the test resulted in mass losses for FCW-Y compared to exposure in air.

- Some ODS Steels Have Much Improved Oxidation Resistance
- Testing of 12Cr ODS-M by Furukawa showed corrosion still a problem
- ODS steels may need additional corrosion protection

Class (III): Refractory Metals and Alloys, Oxygen-Free Pb, up to 1000^{o}C

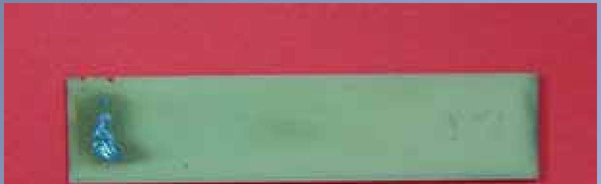
- W, Mo, Ta, Nb - compatible with LBE/Pb
- Oxidation problems arise if oxygen in LBE/Pb is high
- Other obstacles more challenging: fabrication, joining, radiation damages, costs, …

Ta tested in 460^{o}C LBE

Ceramics and Composites, Oxygen-Free Pb

- Compatibility not a key problem - Gangler: "The ceramics and cermets which showed no evidence of corrosion by molten Pb-Bi eutectic alloy are alumina, beryllia, boron carbide, boron carbide + iron, chromium carbide, titanium carbide, and its cermets of nickel and cobalt, magnesia, molybdenum disilicide, NBS 4811c (high beryllia porcelain), fused quartz, silicon carbide bonded with boron carbide, zircon, zirconium carbide + niobium, and zirconia" (J. Am. Ceram. Soc. 37, 312(1954))
- SiC/SiC composite may be the most promising
- Other obstacles more challenging: fabrication, joining, radiation damages and degradation of thermal properties, costs, …

Alumina tested in 520ºC LBE



Alumina tested in 460ºC LBE

A Conceptual Development Path for Lead-Alloy Coolant Technology and Materials