Corrosion Mechanism of T91 (Fe-9Cr) Steel in Pb-Bi Eutectic Alloy aided by Thermodynamic Calculations: Effect of Oxygen

DE LA RECHERCHE À L'INDUSTRIE

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Eurocorr 2020

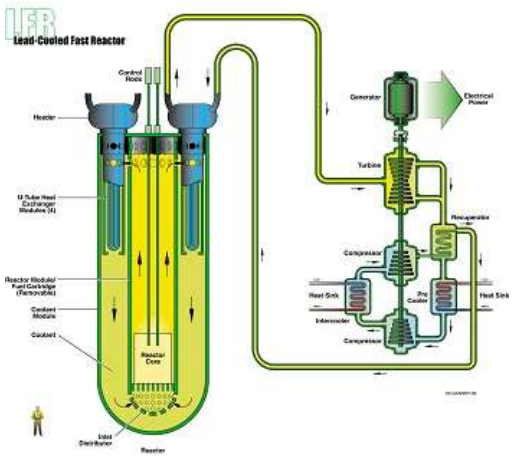
30th June 2020

CONTEXT

CONTEXT: LEAD ALLOYS FOR NUCLEAR REACTORS

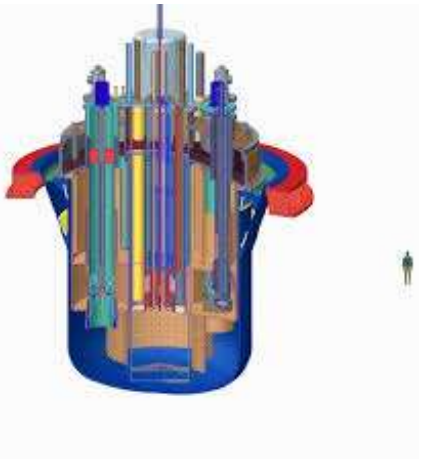
The Fe-9Cr steel is one of the structure material alloy proposed as a candidate for:

- coolant for the Gen IV Lead-cooled Fast Reactor (LFR) with Pb/Pb-Bi Eutectic (LBE),
- spallation target material of the Accelerator Driven Systems (ADS),



LFR design

One of the Generation IV concept



MYRRHA ADS design

Multi-purpose hYbrid Research Reactor for High-tech Applications

Due to **large solubilities** of the major elements of the steel candidates (T91, 316-L), liquid Pb alloys are very aggressive towards the materials for both these nuclear concepts

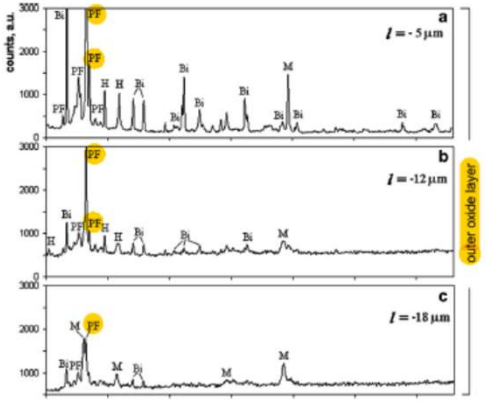
CONTEXT: CORROSION BY LEAD ALLOYS IN NUCLEAR POWER PLANTS

Structural alloys exhibit severe damages when exposed to heavy liquids Pb or Lead-Bismuth Eutectic (LBE) at high temperatures

Generally, **oxidation of martensitic steels (T91/Fe-9Cr)** in pure lead or in Pb-Bi alloy is characterized by the **growth of a duplex Cr-Fe spinel oxide scale** in the temperature range 400°C to 620°C in oxygen saturated LBE.

However Yeliseyeva et al. showed that above 550°C, the oxide scale composition changes to form a **plumboferrite**.

Above 550°C, the interaction mechanism changes from oxidation to liquid metal corrosion: **Dissolution of steel components into the liquid metal coupled with the penetration of melt into the matrix**

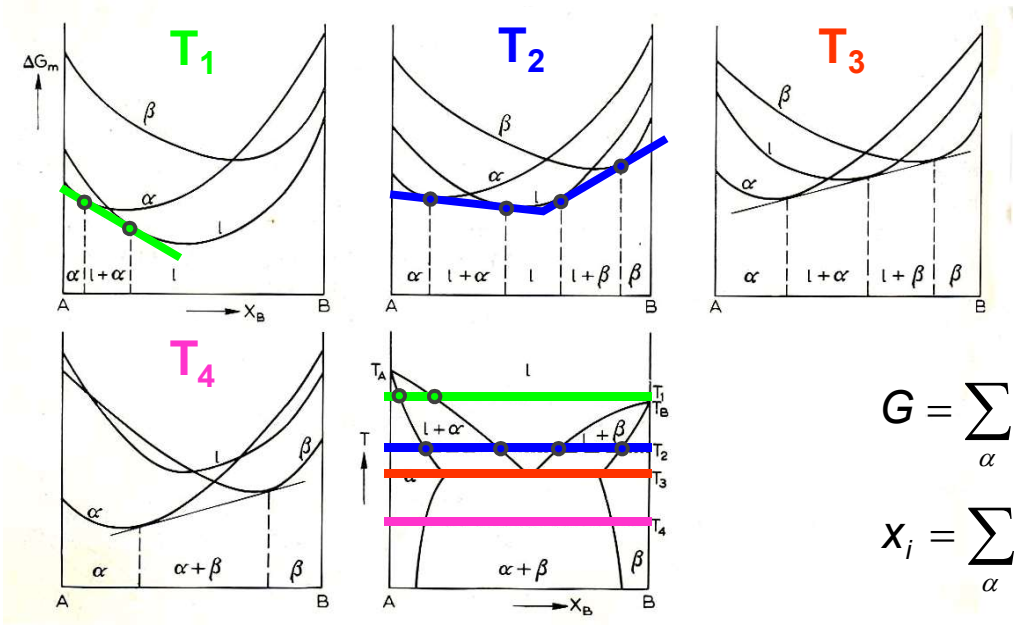


The challenge of this ongoing study is **to predict the thermodynamics** and the kinetics of oxidation and/or dissolution above 600°C

THERMODYNAMIC APPROACH: THE CALPHAD METHOD
THERMODYNAMICS OF SOME LEAD AND LBE SYSTEMS

THE CALPHAD METHOD: RELATION BETWEEN GIBBS ENERGY AND PHASE DIAGRAMS

In a A-B system, **the phase diagram is related to the Gibbs energy functions** of the phases



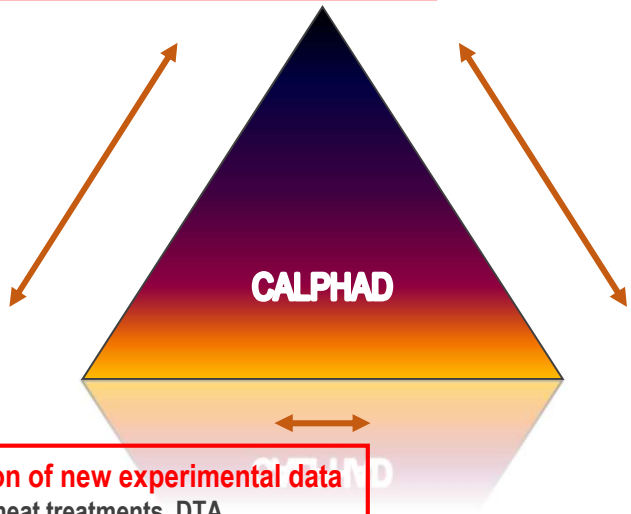
$$G = \sum_{\alpha} m^{\alpha}.G_m^{\alpha}$$

$$x_i = \sum_{\alpha} m^{\alpha}.x_i^{\alpha}$$

$$\min(G) = \min\left(\sum_{\alpha} m^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha} \text{ or } y_k^{(l,\alpha)})\right)$$

THE CALPHAD METHOD: PRINCIPLE OF THERMODYNAMIC MODELING

1st Step: Critical review of literature data



2nd Step: Acquisition of new experimental data

Phase transitions by heat treatments, DTA

ΔH_f, Cp(T), H(T)-H(298K) by **Calorimetry & DSC**

Chemical activities by Knudsen Cell MS, EMF

ΔH_f (@ 0 K) by ab initio calculations

Binary Systems
Ternary Systems

CALPHAD CANNOT PREDICT UNKNOWN PHASES (not entered in the database)

3rd Step: Modeling

Definition of models
Selection of data
Optimising process

1st Modeling: Binaries
2nd Modeling: Ternaries
➡ *Extrapolation towards higher order systems*

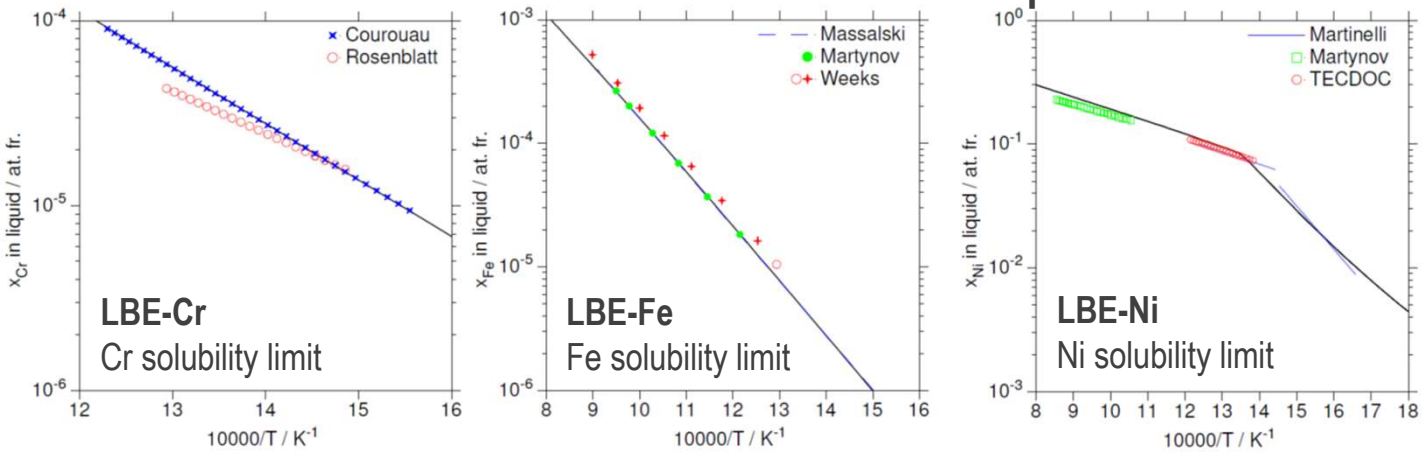
Applications: Phase diagrams & Thermodynamic properties

THERMODYNAMIC APPROACH USING THE CALPHAD METHOD METALLIC SYSTEM

Need to predict **fundamental data** on the equilibrium behavior of the alloys in Pb & LBE

The main systems assessed in the database are: Cr-Ni-Fe – Bi-Pb – O
alloy **coolant** **p(O_2)**

Some calculated solubilities at LBE composition



Ni behavior in molten LBE is the major drawback concerning the use of austenitic stainless steels

- Huge Ni solubility when compared to other metals: about 3 order of magnitude at 673 K
- Very sensitive to T under 738 K due to the steep Bi-rhombo-Bi_3Ni liquidus
- Change slope above 738 K due to the smoother Bi_3Ni-BiNi liquidus

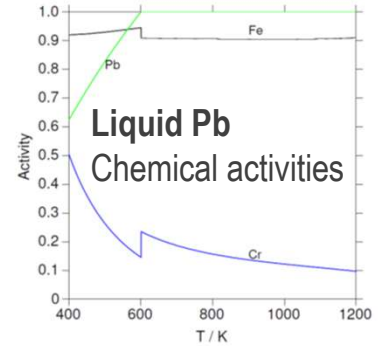
THERMODYNAMIC APPROACH USING THE CALPHAD METHOD METALLIC SYSTEM

Using Calphad calculations, Pb & LBE/structural materials interactions can be predicted

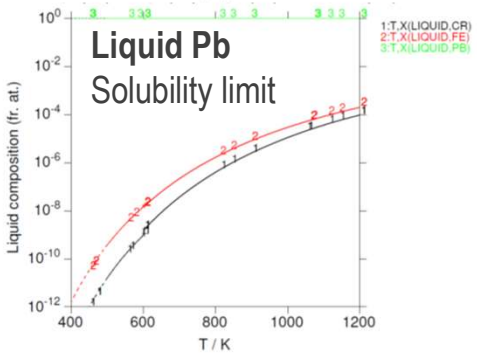
Tableau I–1 : Composition chimique de l'acier T91 donnée en pourcentage massique (Ascometal)

Cr	Mo	Mn	V	Ni	Nb	C	Fe
8,32	0,86	0,48	0,20	0,06	0,06	0,09	Balance

In Pb:

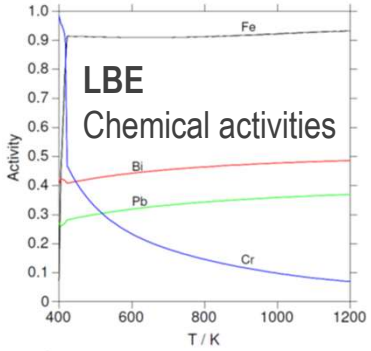


Liquid Pb
Chemical activities

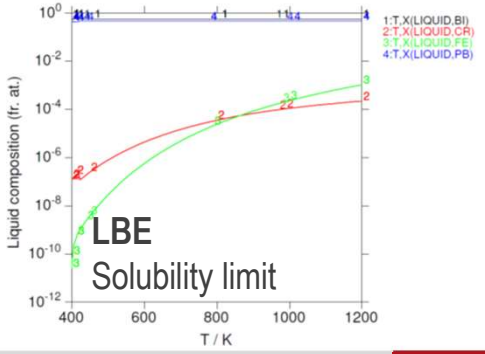


Liquid Pb
Solubility limit

In LBE:



LBE
Chemical activities

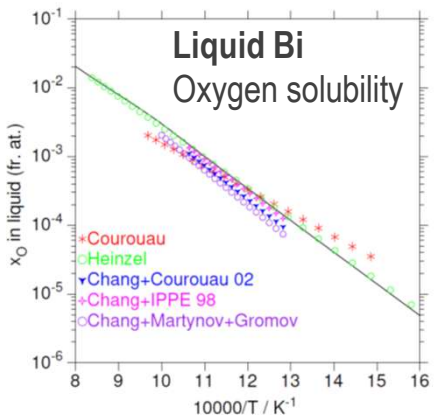


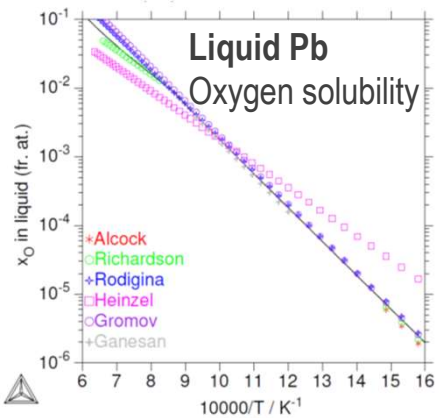
LBE
Solubility limit

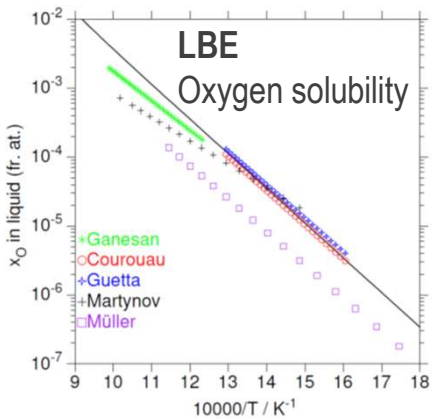
THERMODYNAMIC APPROACH USING THE CALPHAD METHOD
INFLUENCE OF OXYGEN IN THE SYSTEM

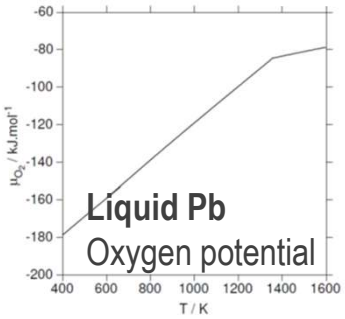
The liquid Pb/steels interactions are determined **by the activity of O in melts**. Depending on its activity, liquid Pb can be a corrosive solvent or a powerful oxidizer.

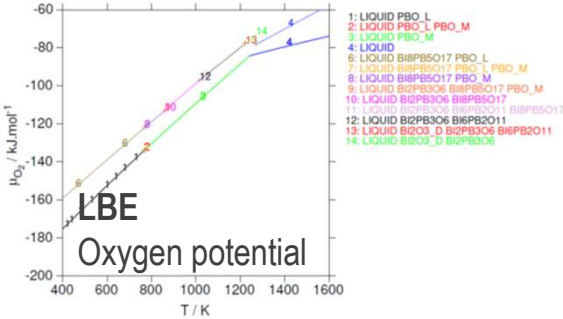
Using Calphad, Pb & LBE/O interactions can be predicted in the Bi-Pb-O system:





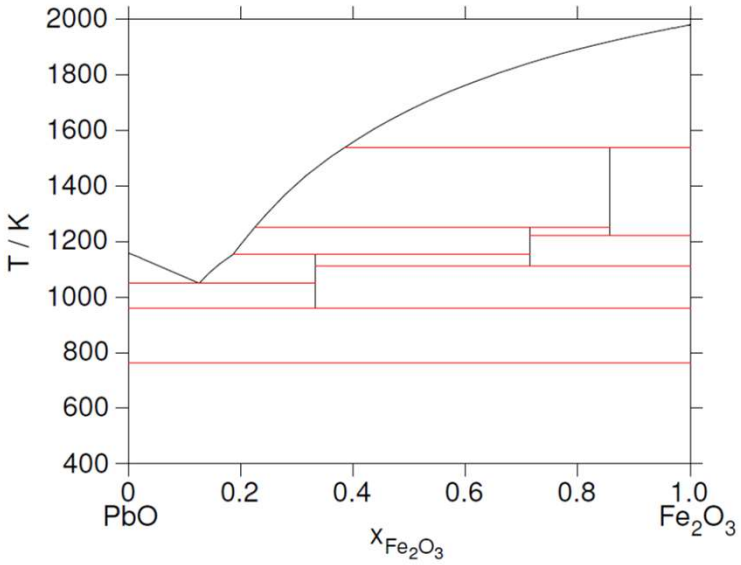


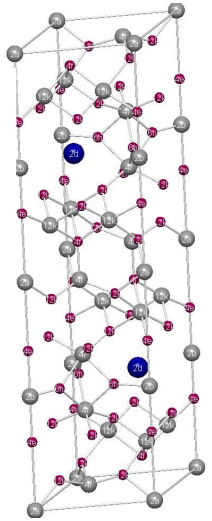




PbO-Fe_2O_3 phase diagram by Diop et al.

3 high temperature ternary oxides: $Pb_2Fe_2O_5$, $PbFe_5O_{8.5}$ & $PbFe_{12}O_{19}$





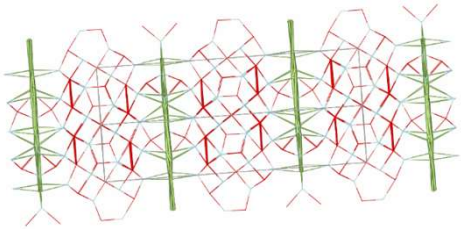
Phase formula **$Fe_{12}PbO_{19}$**

Mineral name magnetoplumbite

Phase prototype $Fe_{12}PbO_{19}$,hP76

Space group $P6_3/mmc$ (194)

$Pb_2Fe_{11}O_{18.33}$: Plumboferrite



In the Fe_2O_3-PbO diagram:

Ternary Fe-Pb-O phases form at high temperature: above ≈600°C

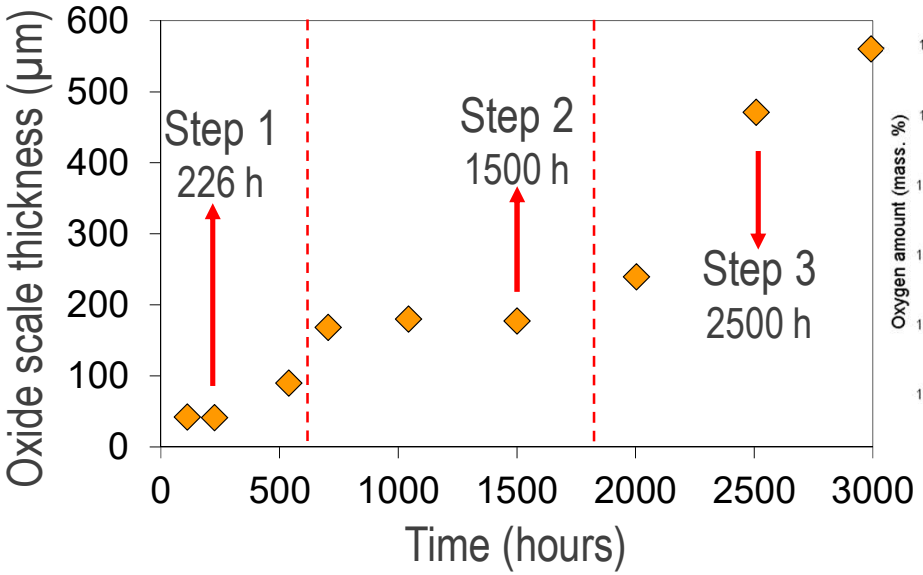
CORROSION MECHANISMS IN STAGNANT LBE SATURATED OXYGEN AT 634°C

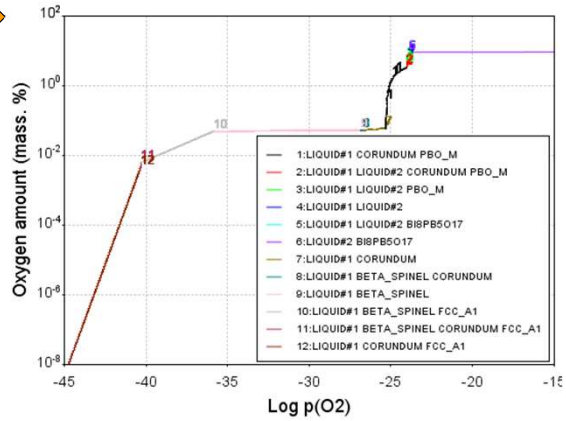
CORROSION MECHANISM
KINETIC STUDY AT 634°C IN OXYGEN SATURATED LBE

Experimental tests reveal 3 corrosion steps during the experiments in static LBE

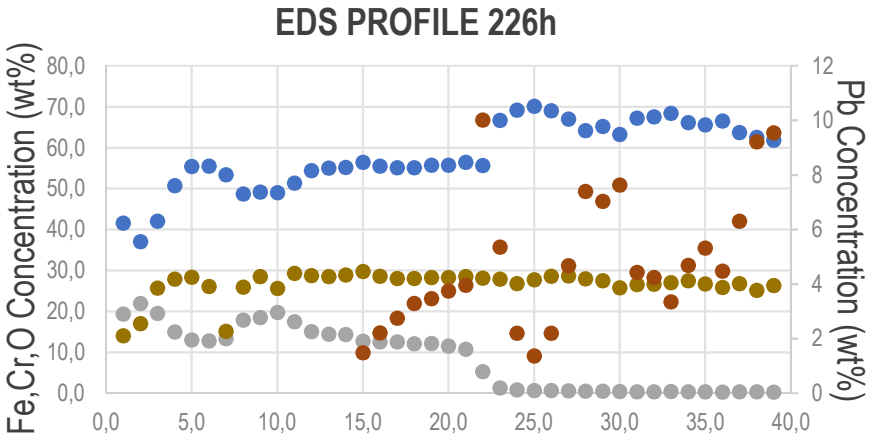
- T=634°C
- Saturated in O_2 using $Ar_{99.95}$ flowing gas

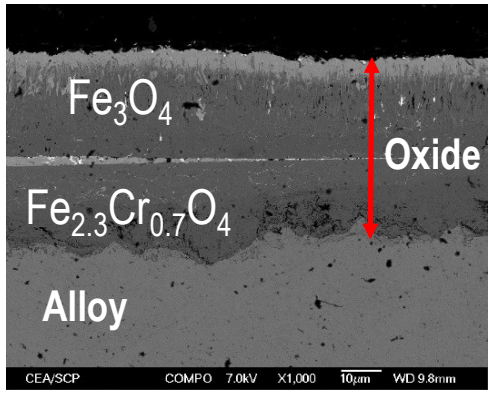
In parallel, some thermodynamic calculations were performed to aid in the understanding of the formed phases

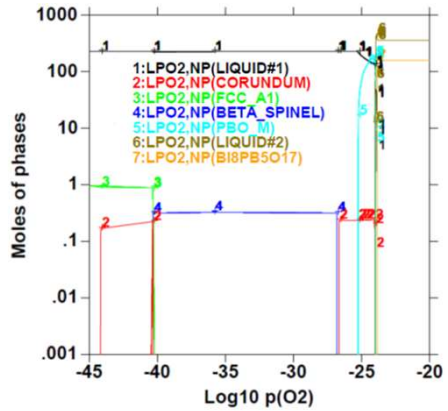




CORROSION TEST IN STATIC LBE UNDER O SATURATED ENVIRONMENT AFTER 226 HOURS







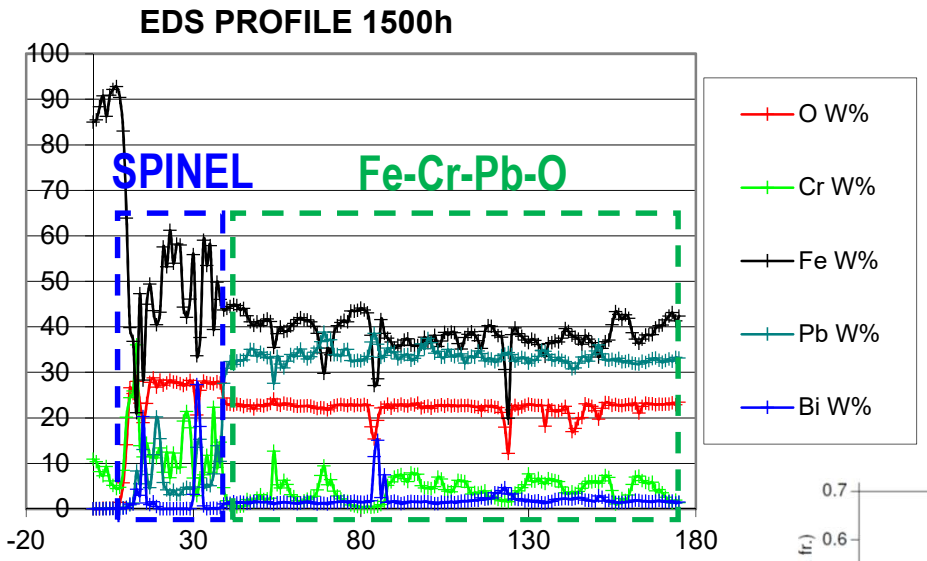
Evolution of the phases at equilibrium as a function of $p(O_2)$:

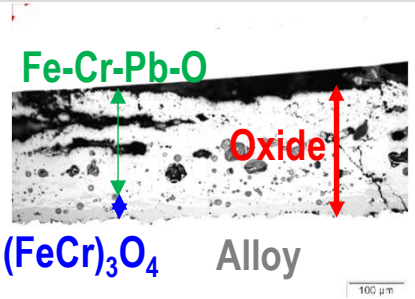
$-45 < \log p(O_2) < -40$: alloy, LBE, corundum Cr_2O_3

$-40 < \log p(O_2) < -27$: alloy, LBE, spinel $Cr_{1.95}Fe_{1.05}O_4$

$-27 < \log p(O_2) < -25$: alloy, LBE, corundum $Cr_{1.6}Fe_{0.4}O_3$

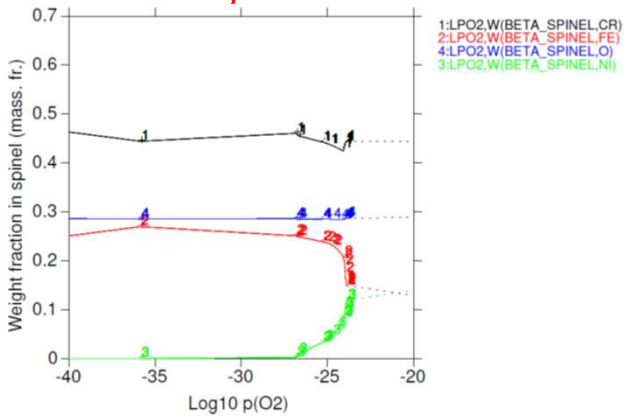
CORROSION TEST IN STATIC LBE UNDER O SATURATED ENVIRONMENT AFTER 1500 HOURS



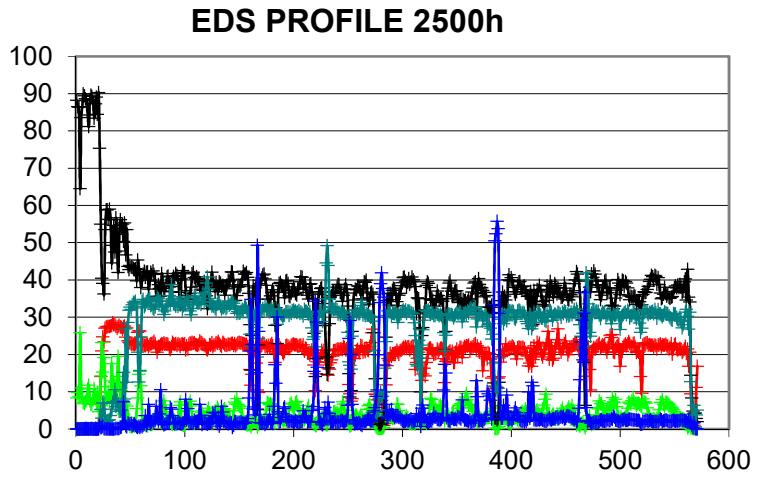


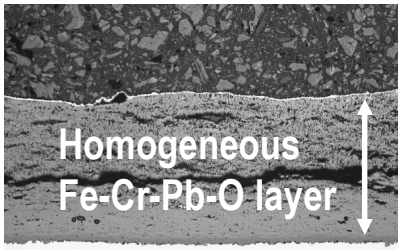
Discrepancies between the measured (Fe rich) and calculated (Cr rich) spinel composition

After 1500 hours: The Pb profile is constant along the oxide scale. **Pb begins to diffuse across the oxide layer**



CORROSION TEST IN STATIC LBE UNDER O SATURATED ENVIRONMENT AFTER 2500 HOURS



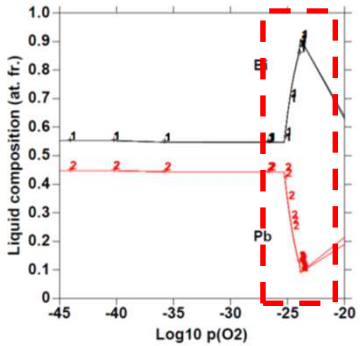


After 2500 hours: The Pb diffused along the oxide layer

The sample undergoes a catastrophic oxidation

Under high $p(O_2)$, the precipitation of PbO depletes the liquid in Pb

The sample undergoes a **catastrophic** oxidation due to an increase of oxygen potential in a **Bi rich metallic liquid**



Conclusion

Thermodynamic calculation can be an helpful tool to evaluate:

In metallic systems:

- The solubilities of structural elements in the molten alloys
- The chemical activities
- The formation of intermetallics (stainless steels, rich in Ni)

In oxide systems:

- Influence of oxygen mass weight on the oxygen potential
- The expected oxide phases: Which one? What composition?
- The effect of PbO precipitation on the LBE liquid enrichment in Bi

Further database developments:

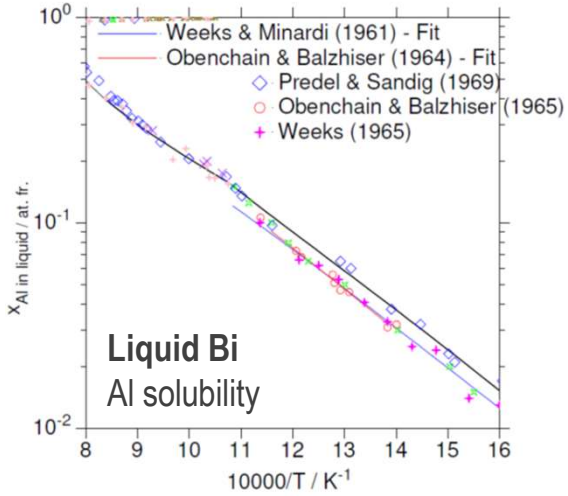
Better description of the Fe-Pb-O ternary phases

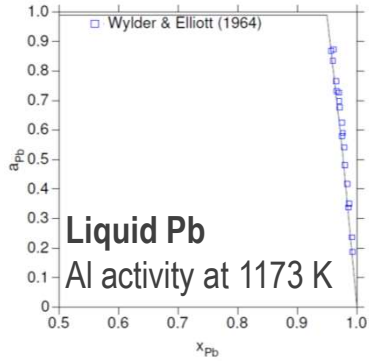
Introduction of Li to consider Pb-Li coolants

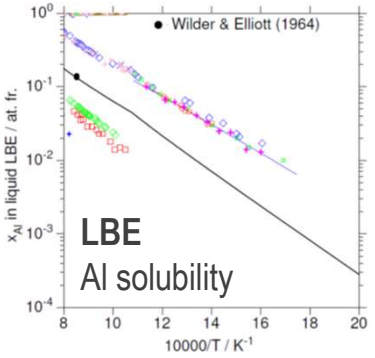
Introduction of U to predict the interactions with the fuel in case of pin failure

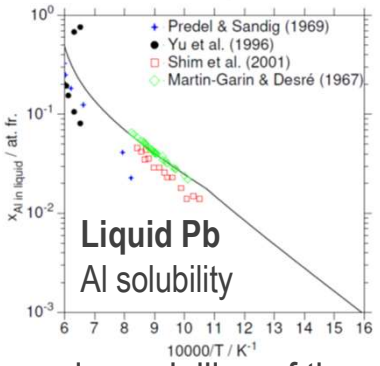
NEW RESULTS 2020: MODELING OF AL SOLUBILITY FOR FECRAL ALLOYS

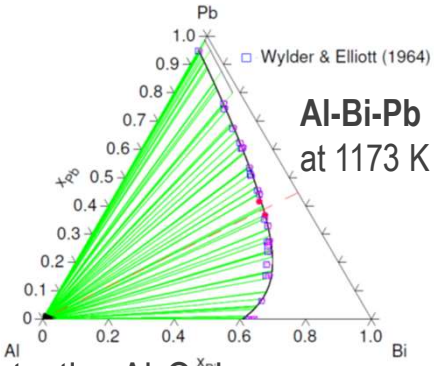
Iron–chromium–aluminum alloys have an excellent corrosion resistance when exposed to Lead and lead–bismuth eutectic environments. As a first step, the solubility of aluminum was recently assessed to address the corrosion behaviors of these alumina-forming alloys under controlled oxygen atmosphere.











Next step will consist in the thermodynamic modelling of the protective Al_2O_3 layers.


cea
Thank you for your attention
Stephane.gosse@cea.fr

CORROSION IN STATIC LBE UNDER O SATURATED ENVIRONMENT
LITERATURE REVIEW ON THE MECHANISM IN MOLTEN LEAD & LBE

According to the literature, the oxidation of martensitic steels in pure molten lead or LBE is characterized by the growth of a duplex Cr-Fe spinel oxide scale for the temperature range from 400°C to 620°C in oxygen saturated LBE

Corrosion mechanism in molten Pb

Materials Science, Vol. 41, No. 5, 2005

CORROSION OF 20Kh13 STEEL IN LEAD MELTS SATURATED WITH OXYGEN

O. I. Eliseeva and V. P. Tsisar

UDC 621.039.534.6:620.193/199

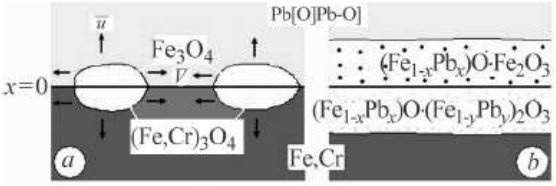


Fig. 4. Schematic diagram of growth of the double oxide layer on the surface of 20Kh13 steel in the lead melt saturated with oxygen ($C_{[O]Pb} = 6 \cdot 10^{-3}$ wt.%) at 650°C.

Corrosion mechanism in molten LBE

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Influence of temperature on the interaction mode of T91 and AISI 316L steels with Pb–Bi melt saturated by oxygen

O. Yeliseyeva [a,*], V. Tsisar [a], G. Benamati [b]

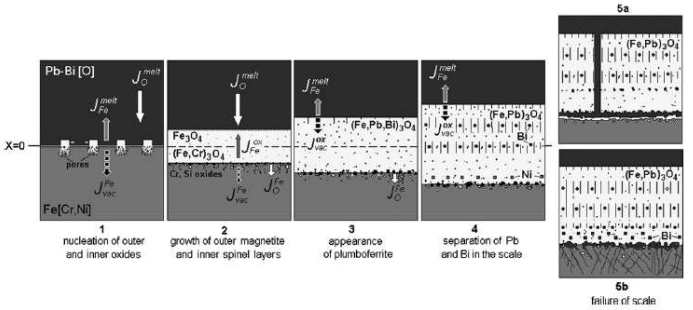
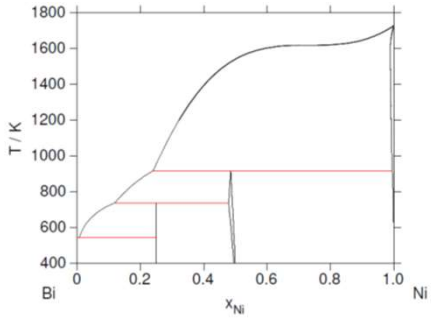
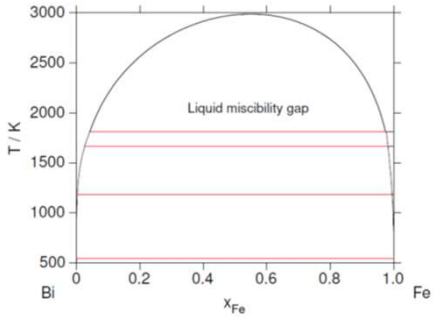
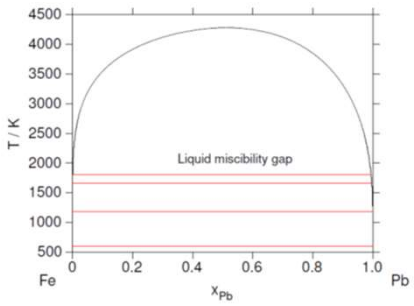


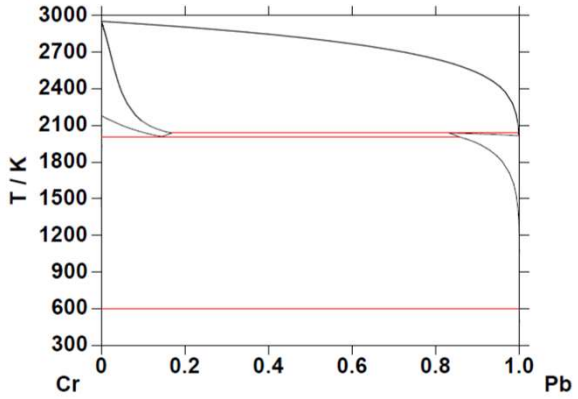
Fig. 11. Kinetic scheme of the double oxide layer evolution on the steel surface under exposure to oxygen-containing Pb–Bi melt.

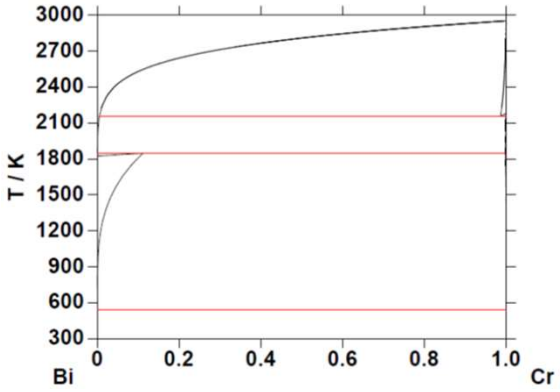
THERMODYNAMIC APPROACH USING THE CALPHAD METHOD
SOME METALLIC SYSTEMS











THERMODYNAMIC APPROACH USING THE CALPHAD METHOD
RICH BI METALLIC LIQUID SATURATED IN OXYGEN