21th International Conference on Nuclear Engineering
ICONE 21
July 29 – August 2, 2013, Chengdu, China

Karlsruhe Institute of Technology
www.kit.edu

www.ipm.lviv.ua

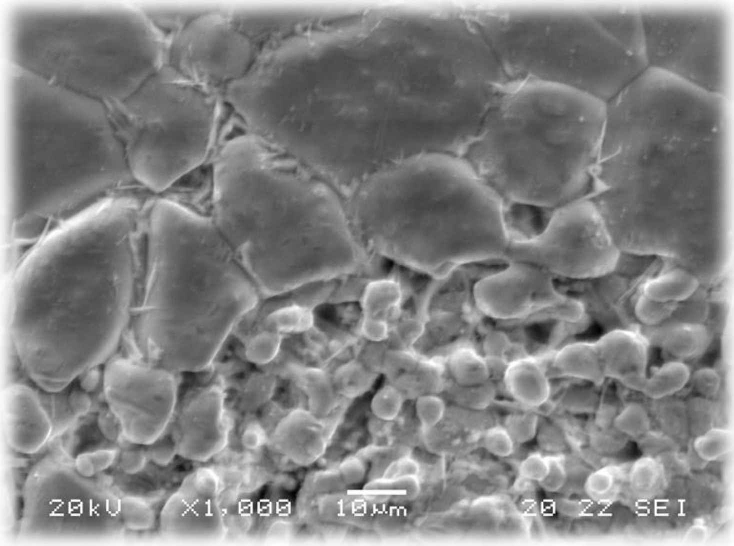
"OXIDATION / DISSOLUTION OF FERRITIC ODS STEELS IN STATIC LEAD WITH VARIOUS OXYGEN CONTENTS AT 650°C"

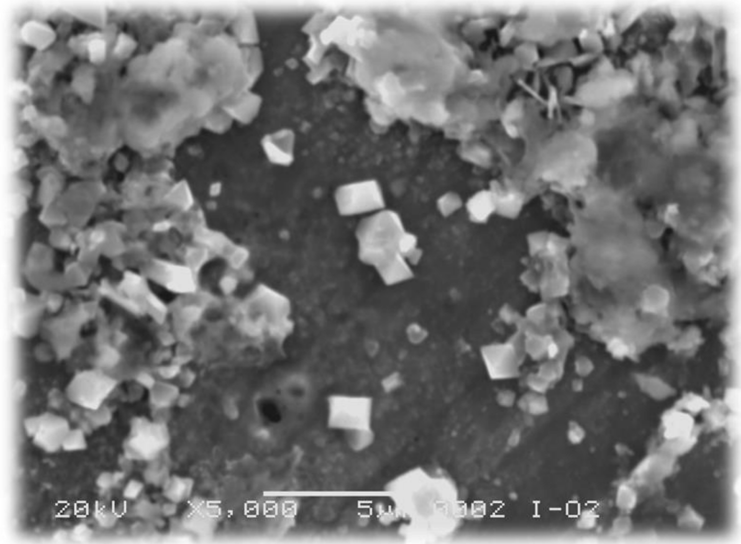
Valentyn Tsisar [a, b], Olga Yeliseyeva [b], Jürgen Konys [a]

valentyn.tsisar@kit.edu

[a] Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[b] Physical-Mechanical Institute (PhMI), 5 Naukova St., 79060 Lviv, Ukraine

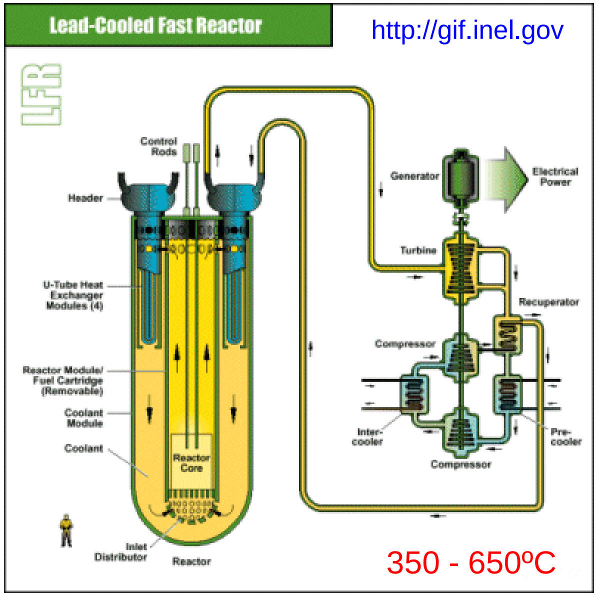


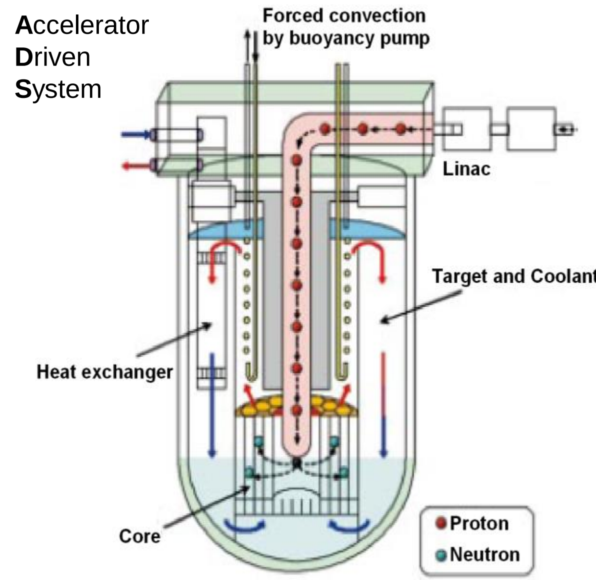


KIT – University of the State of Baden-Wuerttemberg and National Research Center of the Helmholtz Association

PhMI – National Academy of sciences of Ukraine (NASU)

GENERATION IV reactor concepts





Pb / Pb-Bi - coolant and/or spallation target.

Steels – main candidate structural materials with temperature limit of application up to 500°C.

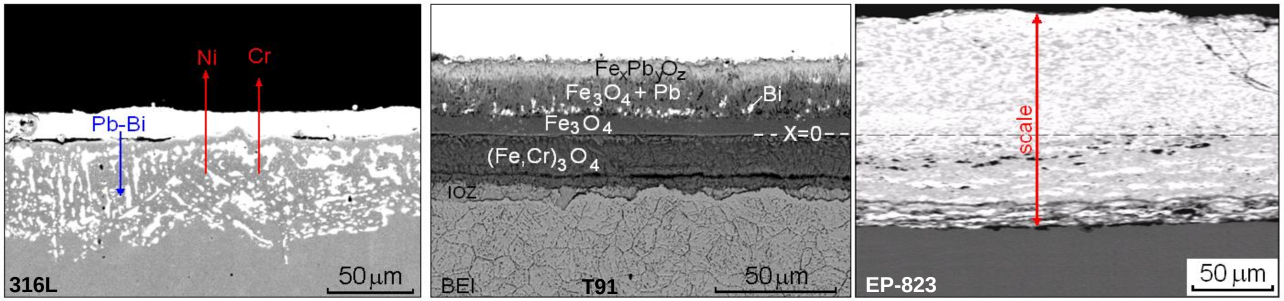
Application of ODS steels allows to increase the operating temperature up to about 700ºC.

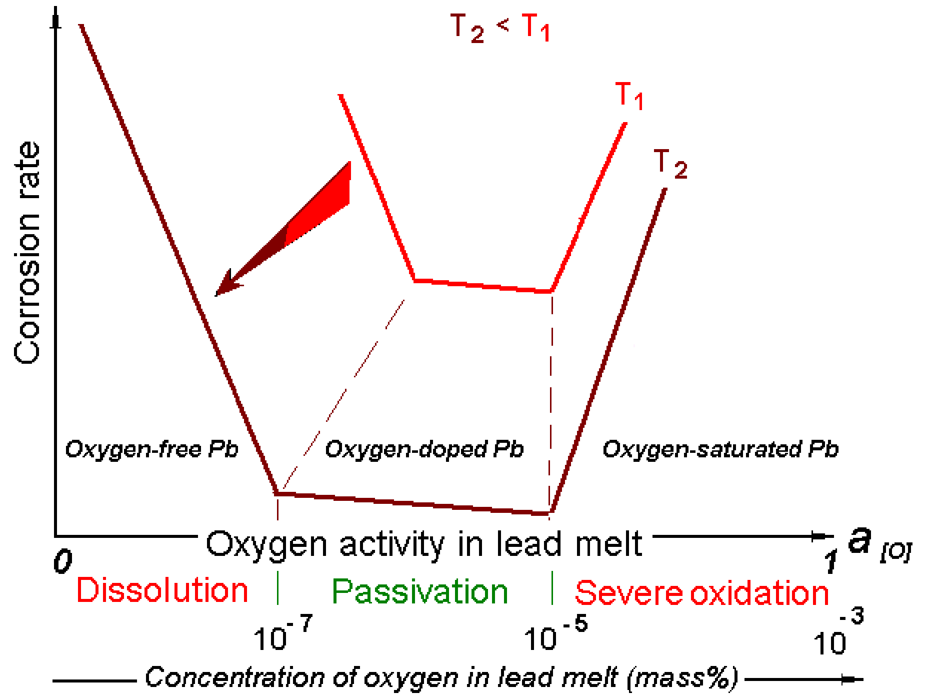
With rise in temperature the corrosion rate of liquid metals with respect to the steels increases !!!

Compatibility of steels with heavy metal melts (Pb, Pb-Bi) - one of the main technological issues of up-to-date reactor material-science !!!

In-situ technology of Pb and Pb-Bi melt doping with oxygen in order to form the protective oxide layer on the surface of steel

Dissolution | **Passivation** | **Severe oxidation**





Schematic representation of corrosion rate and interaction modes of steels in Pb/Pb-Bi melts depending on the oxygen concentration in the liquid metal and temperature.

Outline

1. Materials and Experimental conditions:

1.1. Ferritic Oxide Dispersion Strengthened Steels (ODS);

1.2. Static Pb with different oxygen concentration;

2. Corrosion of ODS steels in:

2.1. Oxygen-saturated Pb melt (~10^{-3} mass%O);

2.2. Oxygen-doped Pb melt (~10^{-6} mass%O);

2.3. "Pure" Pb melt ($\ll 10^{-7}$ mass%O);

3. Summary

1. Materials and Experimental conditions

Ferritic ODS steels

"Frantsevich Institute for Problems of Materials Science" (Kiev, Ukraine) Prof. Ivanova I.I.

- Fe-13Cr-2Mo(TiO_2)
- Fe-13Cr-2Mo-2Si(TiO_2)
- Fe-13Cr-2Mo(Y_2O_3)
- Fe-13Cr-2Mo

HIPing followed by extrusion from the temperature 1200°C or cold-rolling

University of Science and Technology (Beijing, China) Prof. Zhangjian Zhou

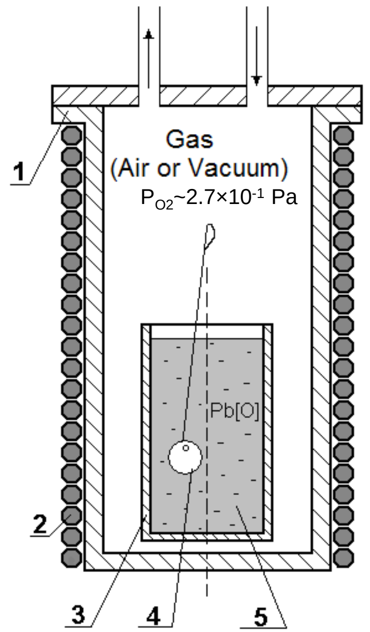
- Fe-14Cr-2W(Y_2O_3)
  Low activated steel

as HIPed state

Structural and compositional differences of steels investigated

- Small composition variations due to alloying by Mo, W and Si;
- The grain size of Fe-14Cr-2W ODS steel was about two times smaller than that in Fe-13Cr-2Mo ODS steels and averaged 800 nm and 2 µm respectively;
- The sufficient number of comparable large (~ Ø 1.0 µm) oxide particles composed of Cr and Ti were detected in the composition of Fe-13Cr-2Mo ODS steels in addition to the nano-sized oxides.

Principal scheme of corrosion test device



1 - Vacuum apparatus
2 - Heaters
3 - Alumina crucible
4 - Sample
5 - Pb- melt

Test conditions

Pb mass% O	Exposure time, h	
	Fe-13Cr-2Mo	Fe-14Cr-2W
oxygen-saturated ~10^{-3} mass% O	200, 500, 1000	-
oxygen-doped ~10^{-6} mass% O	500, 1000, 1750	1000
pure ≤ 10^{-14}	-	1000

MA+HIP

test in Pb

as-received

- drilling;
- polishing;
- marking;
- thermal treatment
900°C, 30 min

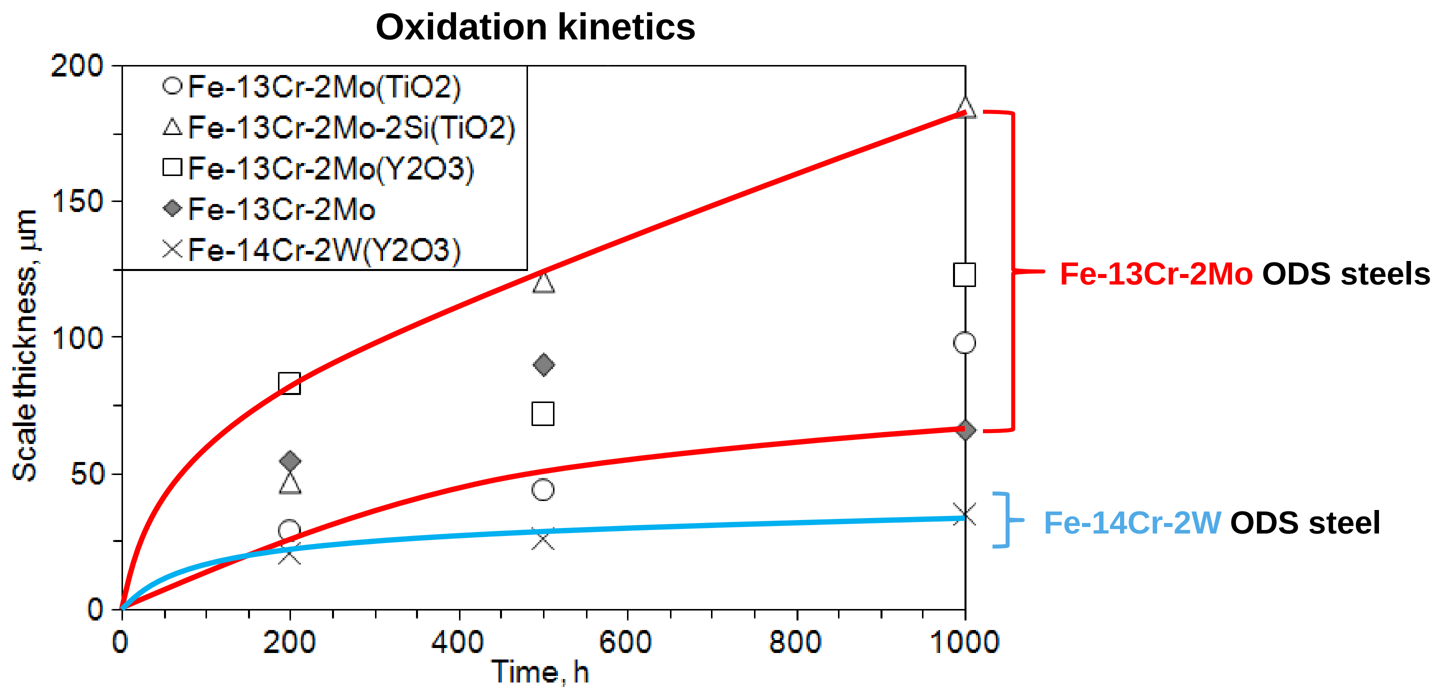
650°C

chemical cleaning to remove Pb

LOM
SEM
EDX
XRD
XPS
HV

Karlsruhe Institute of Technology

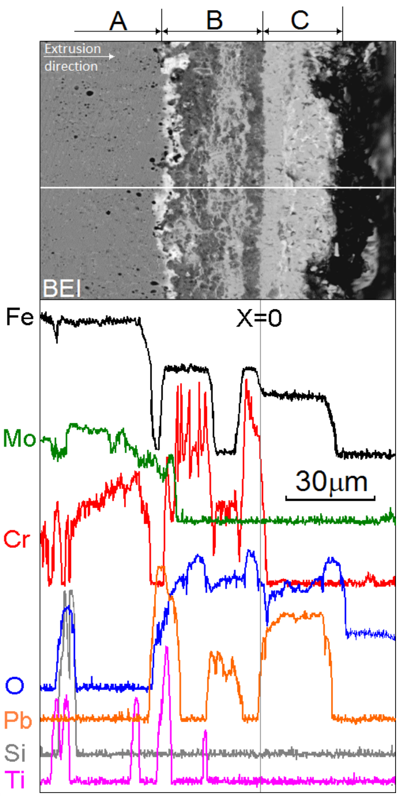
2.1. Corrosion test in Oxygen-saturated Pb melt (~10^{-3} mass%O) at 650°C



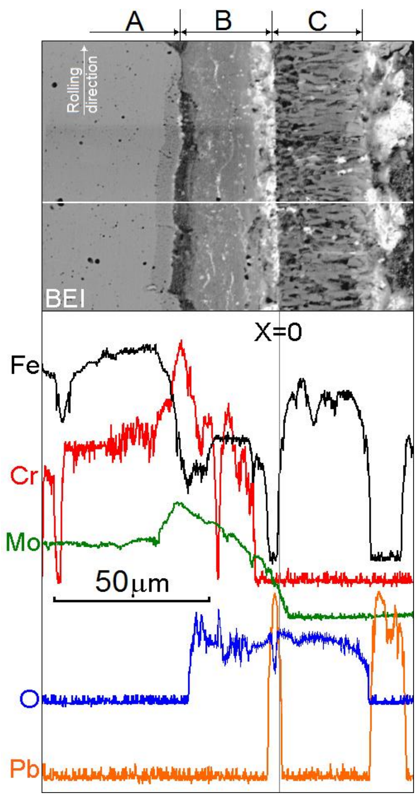
- **Fe-13Cr-2Mo steels oxidize much more intensively than Fe-14Cr-2W;**
- **Difference in the oxidation response cannot be explained by the minor variations in the alloying with Mo or W and/or slightly larger Cr content in the latter steel, especially under the given - high oxidizing conditions (oxygen-saturated Pb);**
- **The effect of microstructure of steels resulting in the different grain size and formation of textures due to manufacturing prehistory might be responsible for different oxidation rate.**

Morphology and composition of scales formed on the surface of **Fe-13Cr-2Mo** ODS steels in oxygen-saturated Pb melt at 650°C.

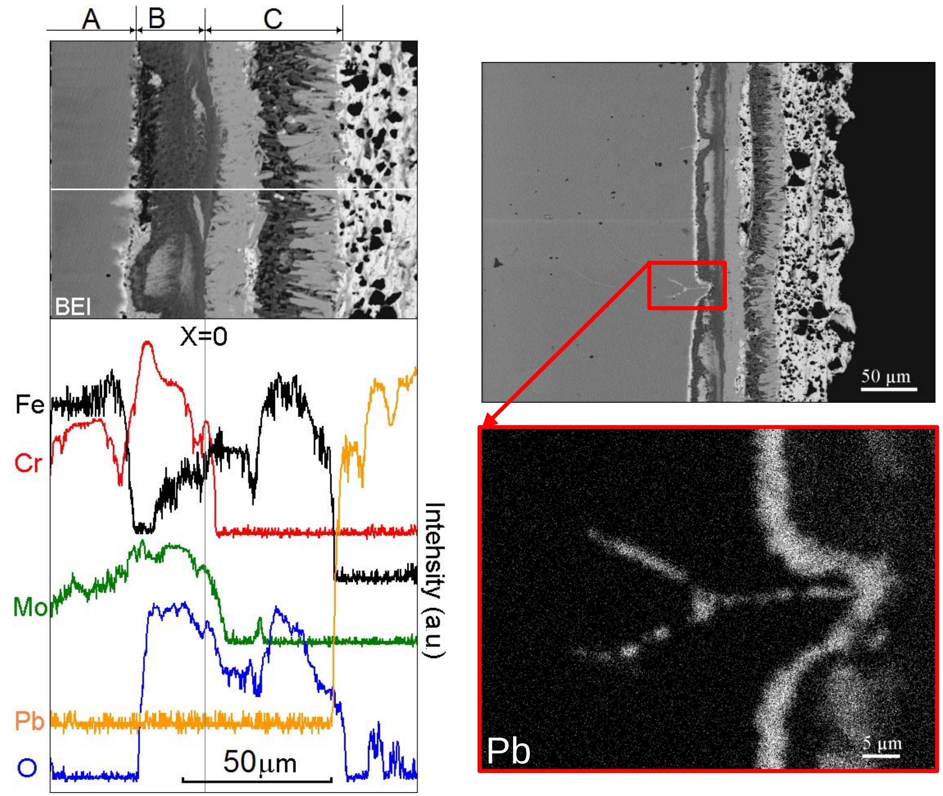
A – steel; **B** – inner spinel; **C** – outer magnetite; **B + C** = bi-layer scale. **X=0** – initial "solid metal – liquid metal" interface.



Fe-13Cr-2Mo-2Si(TiO_2)
200 h



Fe-13Cr-2Mo(Y_2O_3)
200 h

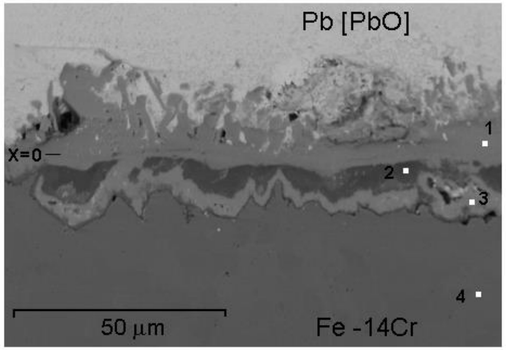


Fe-13Cr-2Mo
500 h

- **Bi-layer magnetite/spinel scale is formed;**
- **Metal recession averages 60÷65 μm after 1000 h.**

Morphology and composition of scale formed on the surface of **Fe-14Cr-2W** ODS steels in oxygen-saturated Pb melt at 650°C.

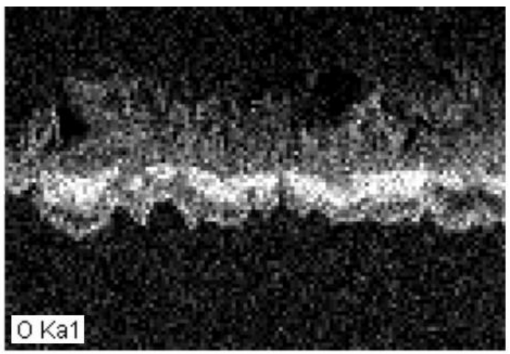
1 – outer magnetite; **2, 3** – inner spinel; **4** – steel. **X=0** – initial “solid metal – liquid metal” interface.



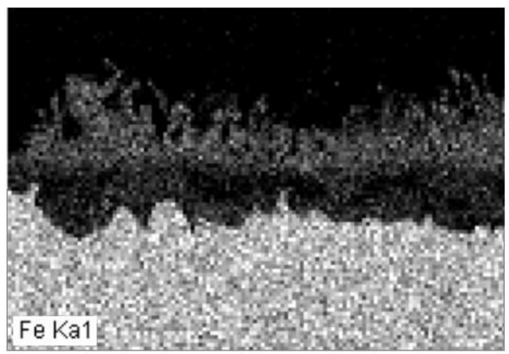
a

Area	Elements, wt. % / at. %					Phase
	O	Cr	Fe	W	Pb	
1	23.20 59.68	–	44.63 32.88	–	32.17 7.44	$PbO\cdot Fe_2O_3$
2	32.78 62.90	43.19 25.50	19.86 10.96	1.02 0.17	3.16 0.47	$FeO\cdot Cr_2O_3$
3	22.73 58.52	17.09 13.54	28.92 21.33	0.89 0.58	30.36 6.04	$PbO\cdot(Fe,Cr)_2O_3$
4	–	12.66 13.68	86.04 85.95	1.24 0.38	–	matrix

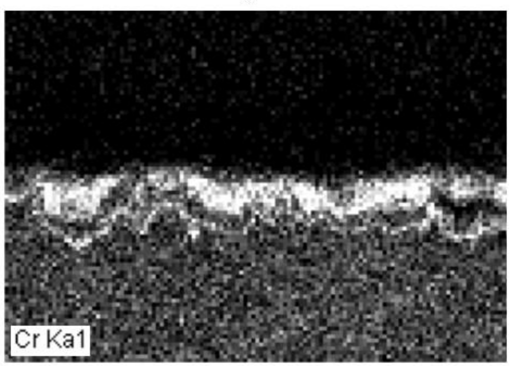
b



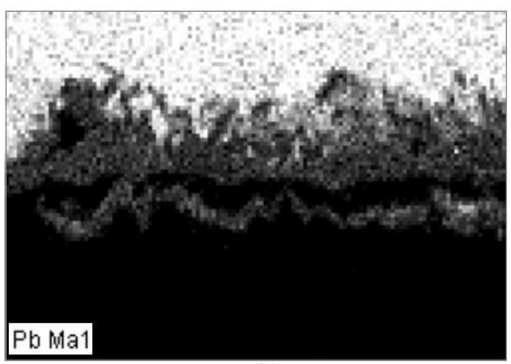
c



d



e



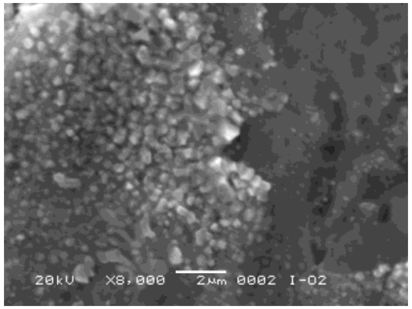
f

- **Bi-layer magnetite/spinel scale is formed;**
- **Thickness of scale reached ~15 μm;**
- **Concentration of Cr in the spinel for Fe-14Cr-2W(Y_2O_3) steel reached ~ 43 mass% while corresponded values for Fe-13Cr-2Mo ODS steels do not exceed ~ 25 mass%;**
- **Metal recession averages 15 μm after 1000 h, i.e. four times smaller than that for Fe-13Cr-2Mo steels.**
- **Pb severely penetrating bi-layer scale.**

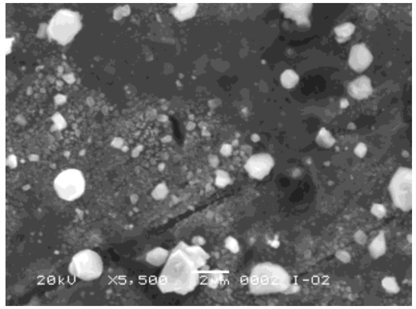
Oxygen-saturated Pb melt (~10^{-3} mass%O) at 650°C

2.2. Corrosion test in Oxygen-doped Pb melt (~10^{-6} mass%O) at 650°C

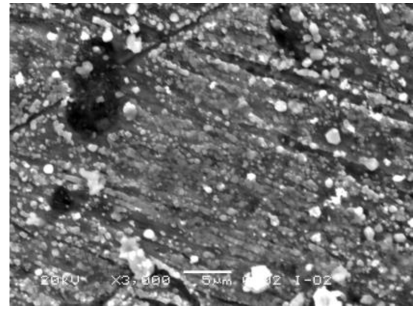
Plan view of the passivated surface of **Fe-13Cr-2Mo** ODS steels after exposure to oxygen-doped Pb melt at 650°C for 1000 h.



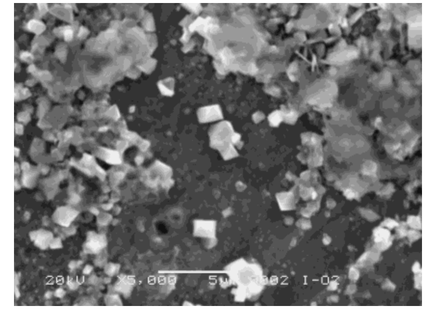
Fe-13Cr-2Mo(TiO_2)



Fe-13Cr-2Mo-2Si(TiO_2)

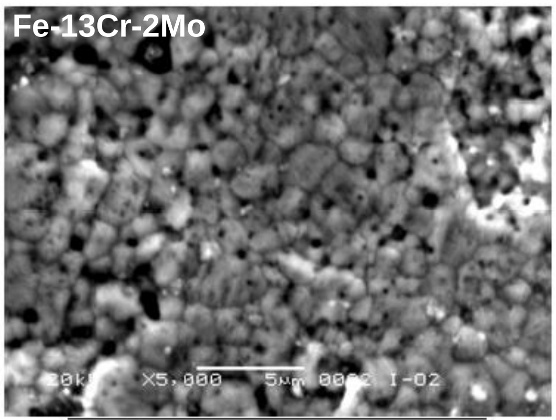


Fe-13Cr-2Mo(Y_2O_3)

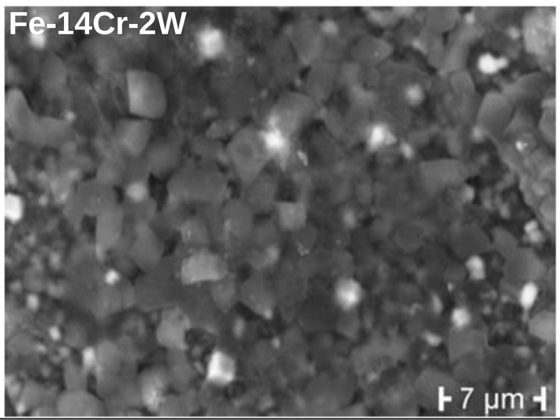


Fe-13Cr-2Mo

Sub-oxide layers are depleted in Cr.



Si	Cr	Fe	Mo
0.24	5.98	92.99	0.79



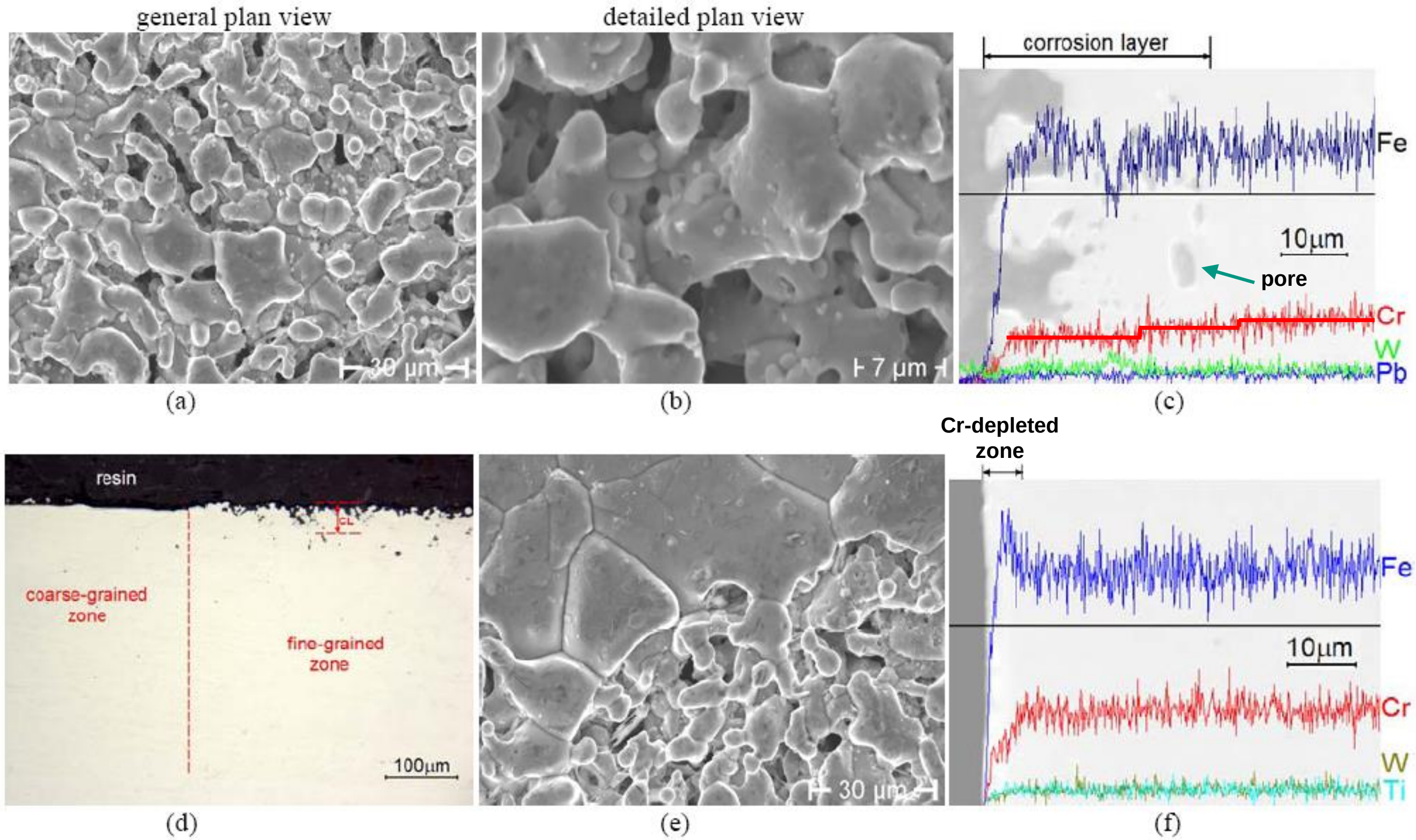
O	Ti	Cr	Fe	W	Pb
51.58	0.62	35.27	6.82	1.61	4.10

Aggregation of the fine crystallites 2.5 μm.

- **Thin Cr-based oxide films (~2 μm) is formed instead of Fe-based bi-layer scale with decrease in oxygen concentration in the melt from ~ 10^{-3} to ~10^{-6} mass%O;**
- **Cr-based oxide film is composed of aggregation of the fine crystallites;**
- **Sub-oxide layers are depleted in Cr;**
- **Outer Cr-based film formed on the surface of Fe-14Cr-2W(Y_2O_3) steel is more dense and uniform in comparison with these formed on the Mo-alloyed steels.**

2.3. Corrosion test in "Pure" Pb melt (<< 10^{-7} mass%O)

Morphology (a, b, e - plan view; d – cross-section) and elemental profiles (c, f) of corrosion zones formed in the near-surface layers of **Fe-14Cr-2W(Y_2O_3)** steel exposed to "pure" Pb melt at 650°C for 1000 h. CL – corrosion layer.



- **Deep-pronounced corrosion attack is observed (Fig. a, b);**
- **Samples showed marked weight losses averaging 92 g/m^2 after 1000 h;**
- **The total depth of corrosion layer, including surface area characterized by the marked ablation of material reached ~ 40 µm (c);**
- **Concentration of Cr in the corroded zone gradually decreased towards surface from 14 mass % to ~ 9 mass %;**
- **Contrary to the corrosion behavior of fine-grained domain, the coarse-grained one did not reveal any substantial corrosion damage (d, e), However, Cr-depletion was also observed in the near-surface zone (~5 µm) (f).**

SUMMARY

- The interaction mode of ODS steels changed from intensive oxidation in the oxygen-saturated melt, accompanied by the formation of a bi-layer magnetite/spinel scale, to formation of a thin protective Cr-based oxide film in the oxygen-doped melt and to the severe steel dissolution in oxygen-free lead;
- It was shown that the Cr-based oxide layer can be formed *in-situ* on the surface of 13-14 Cr ODS steels in static oxygen-doped (~10^{-6} mass%O) Pb melt at 650°C instead of bi-layer Fe-based scale;
- The specific phase-structural state of ODS steels (fine-grained structure, dispersion oxide particles (TiO_2, Y_2O_3)) is favorable for the formation of Cr-rich oxide layer in oxygen-doped Pb at 650°C;
- In the pure liquid Pb, ODS steels in turn underwent severe liquid metal corrosion attack and moreover, fine-grained structure of ODS steels, in this case, appeared to be more vulnerable to the general corrosion than coarse-grained;
- Increase in oxygen concentration (~10^{-3} mass%O) resulted in intensive oxidation accompanied by the formation of non-protective bi-layer Fe-based scale severely damaged by Pb.

Thank you for attention !!!

ACKNOWLEDGMENTS

Authors are thankful to:

- Prof. Ivanova I.I. from “Frantsevich Institute for Problems of Materials Science” (Kiev, Ukraine) and Prof. Zhangjian Zhou from University of Science and Technology (Beijing, China) for materials supplying;
- Authors express thankful to Dr. Carsten Schroer for valuable comments and discussion of the results presented.