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WP5 Safety evaluation of the chemical plant

Corrosion study of YSZ and Hastelloy in FLiNaK and LiF-ThF_4

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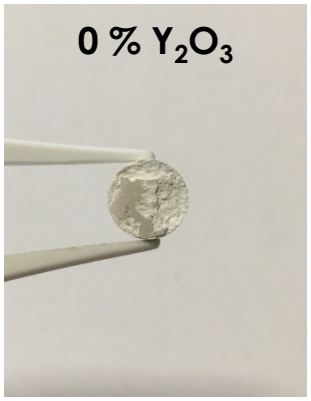
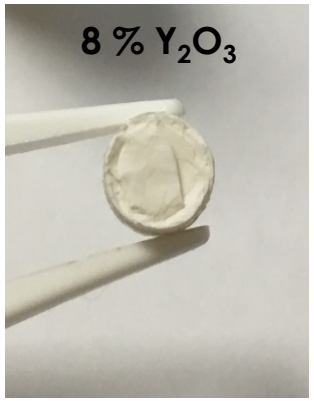
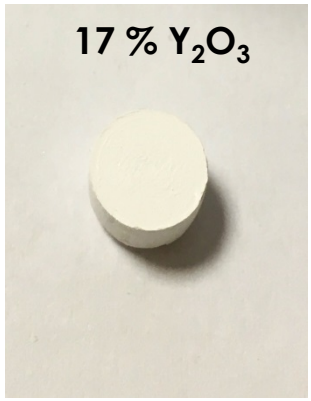
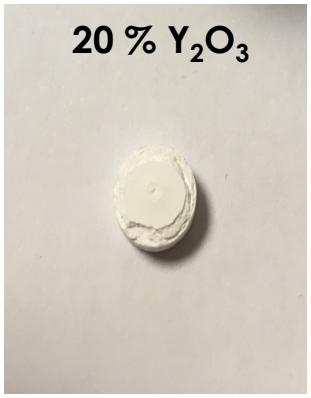
Corrosion of YSZ (Yttria-stabilized zirconia) and Hastelloy substrates in LiF-ThF_4 at 750 °C

- All samples were provided by CINVESTAV institute, Mexico.
- ZrO_2 pellets dopped with Y_2O_3 (x %)









- Hastelloy B2 substrates with a coating of YSZ

Ni	**69.24 %**
Mo	**27.68 %**
Fe	0.96 %
Mn	0.66 %
Cr	0,11 %
Co	< 0.02 %
Si	< 0,005 %

- All pellets were sintered at 1300 °C in air.

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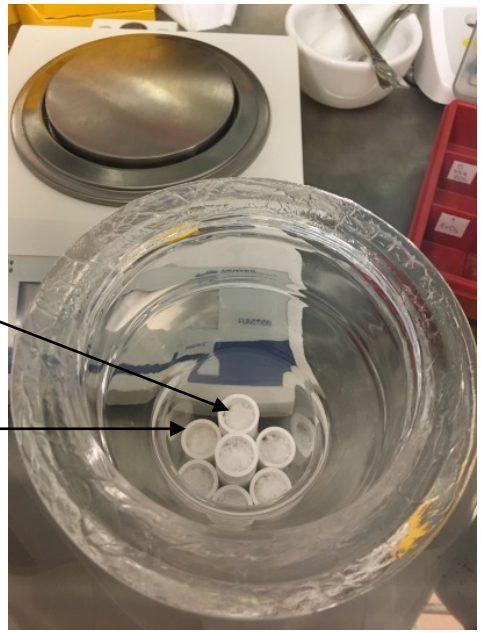
Experimental approach

- Samples preparation in an inert glove box under argon atmosphere



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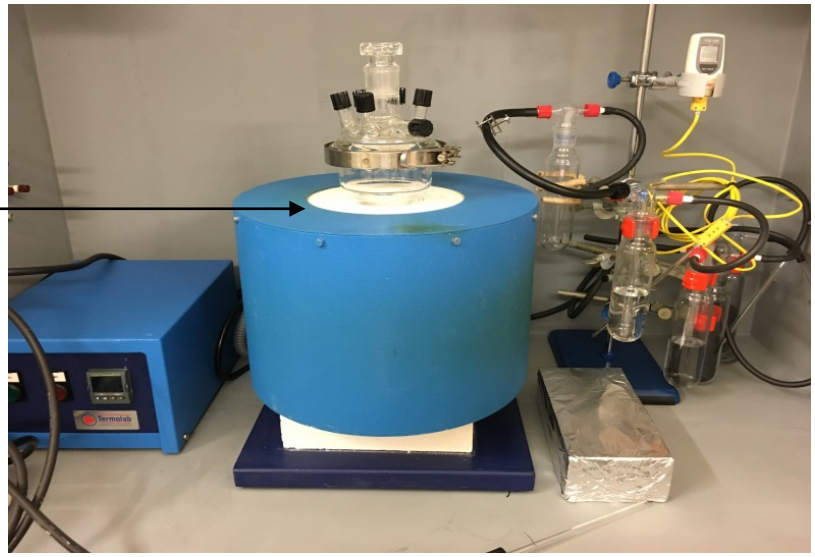
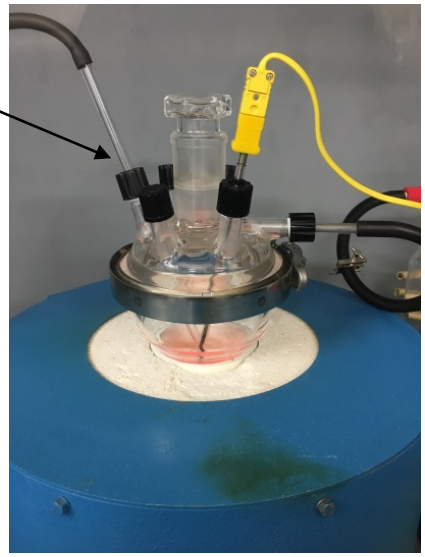
Experimental approach

- Corrosion test : 40 days at the equilibrium potential of the molten salt.

T = 750 °C



Ar atmosphere



- Due to technical problems corrosion test :
  - 15 days (YSZ (8, 11.3 and 17 mol %) samples)
  - 40 days (ZrO_2, YSZ (20 mol %) and both hastelloy substrates)

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Experimental approach: Characterization

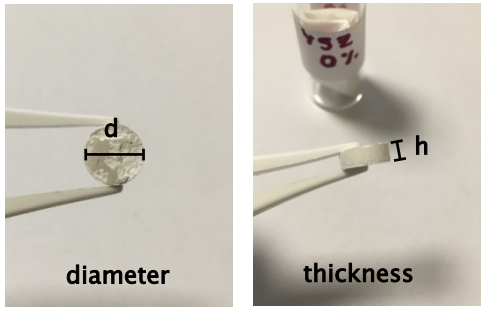
Thermodynamic Calculation

⇩

Pellets and Hastelloy samples

Physical measeurements

- Samples sizes



- Weight ⇨ Weight loss

Confocal microscopy

X-ray diffraction (XRD)

Molten salt

X-ray diffraction (XRD)

Inductively coupled plasma (ICP)

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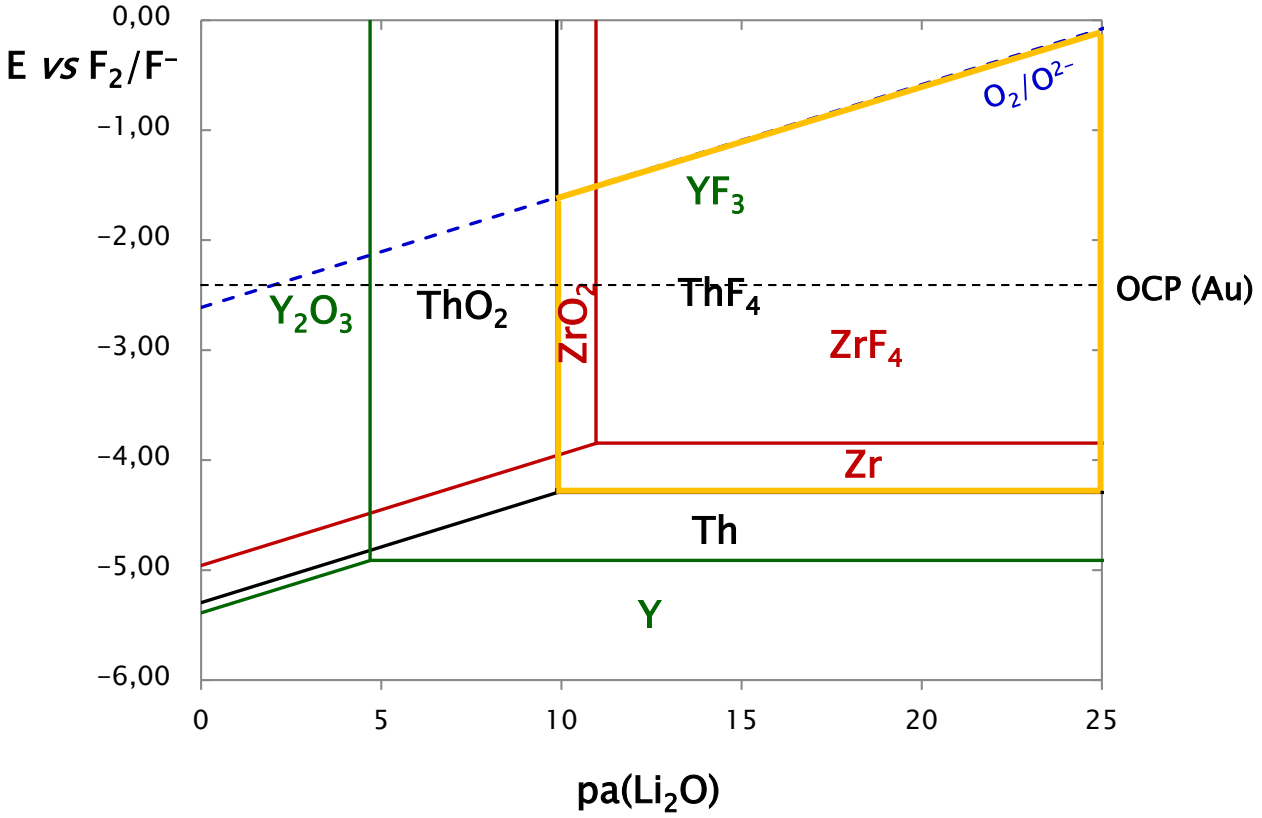
Thermodynamical stability of zirconium and yttrium in LiF-ThF_4 at 750 °C

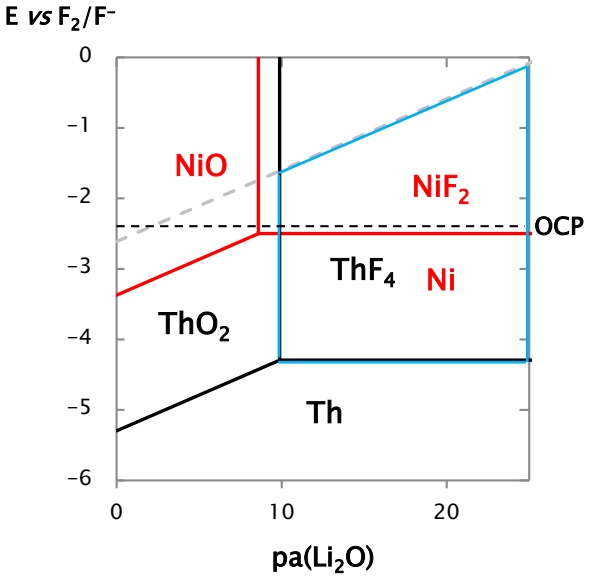


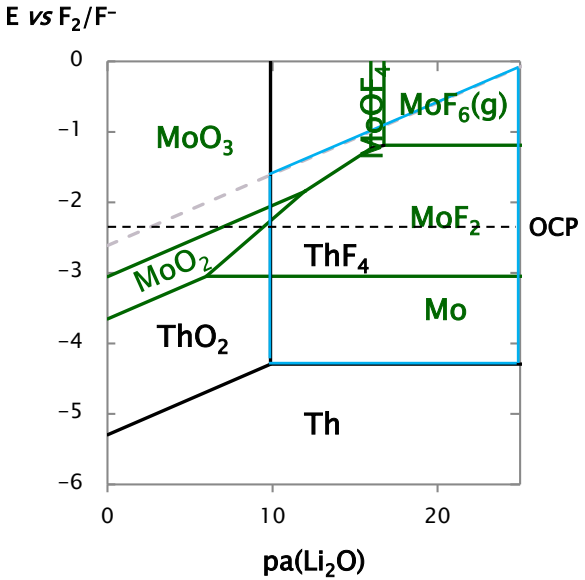
- Chemical oxidation of Y_2O_3 in presence of THF_4:

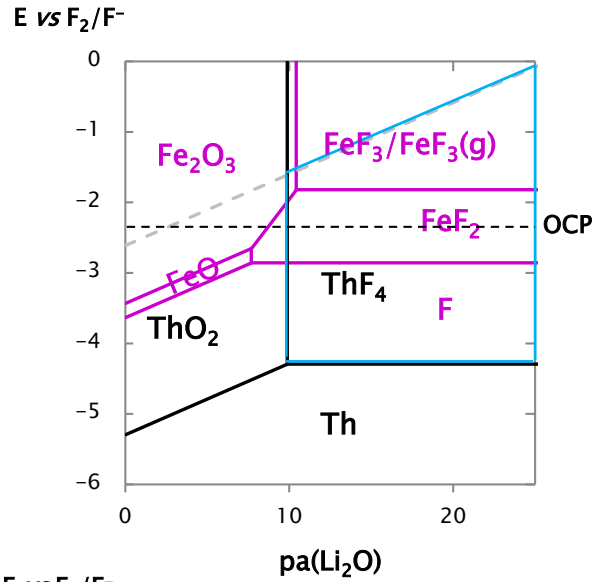
$$6ThF_4 + 4Y_2O_3 \rightarrow 6ThO_2 + 8YF_3$$

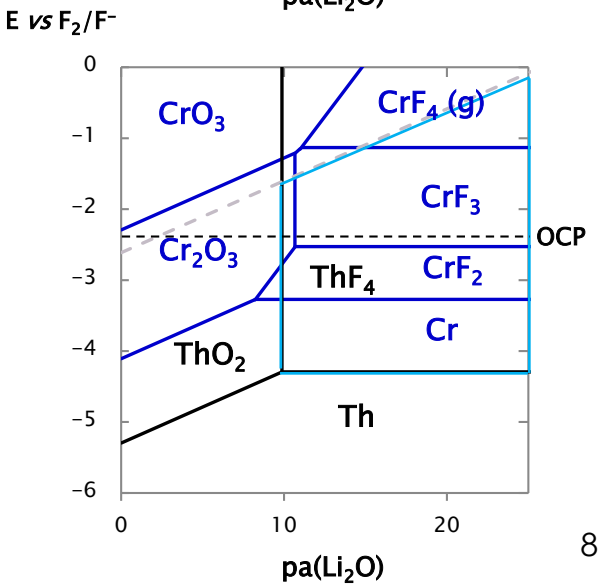
$\Delta G_{(750\ °C)}$ = -822,879 kJ

Thermodynamical stability of metallic elements presents in Hastelloy at 750 °C



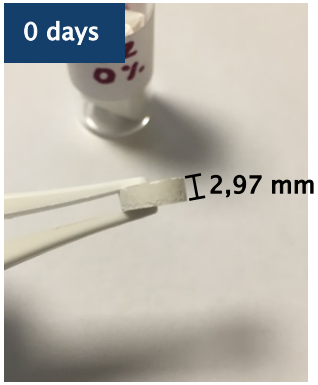
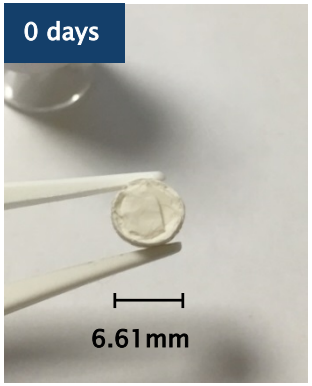
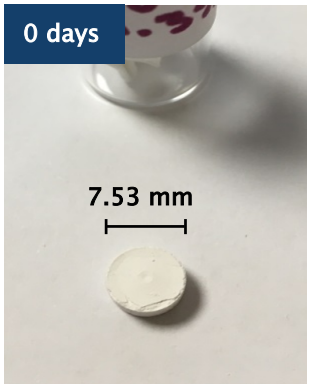
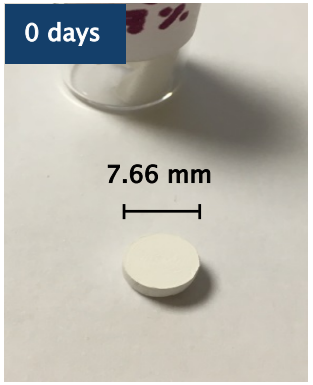
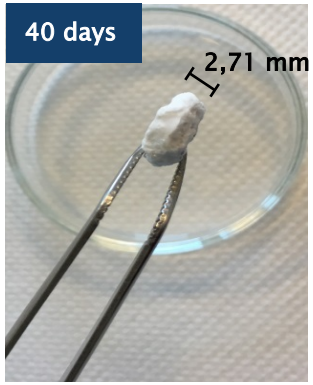
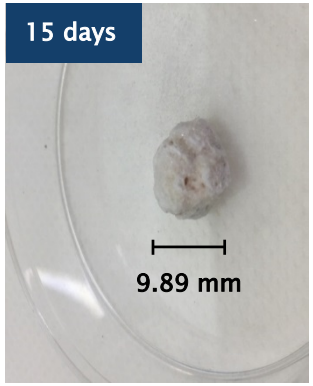
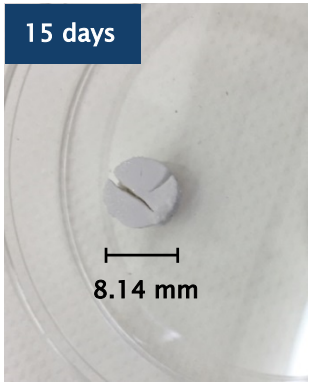
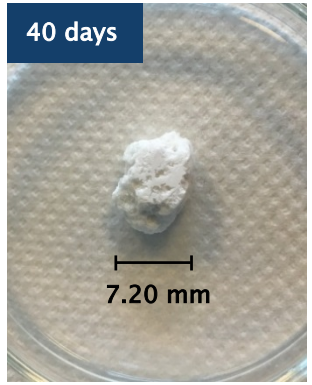






- Nickel, molybdenum, chromium and iron are oxidized

Corrosion of YSZ in LiF-ThF_4 at 750 °C

ZrO_2 pellet	ZrO_2 8 mol % Y_2O_3	ZrO_2 11.3 mol % Y_2O_3	ZrO_2 17 mol % Y_2O_3	ZrO_2 20 mol % Y_2O_3
				
				

15 or 40 days

- Degradation surface of all pellets
- Samples are covered partially or totally by LiF-ThF_4
- Weight loss measurement were not possible

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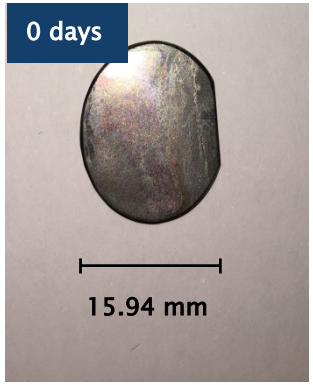
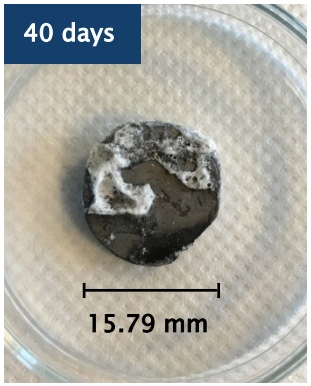
Corrosion of Hastelloy substrates in LiF-ThF_4 at 750 °C

Hastelloy (ZrO_2 - 17 mol % Y_2O_3)



Hastelloy (ZrO_2 - 17 mol % Y_2O_3 + 10 mol % C)



40 days

- Modification of the Hastelloy surface
- Hastelloy substrates have lost its initial coating
- Gray and black regions on both surfaces
- A lot of recrystallized salt remain in Hastelloy surface

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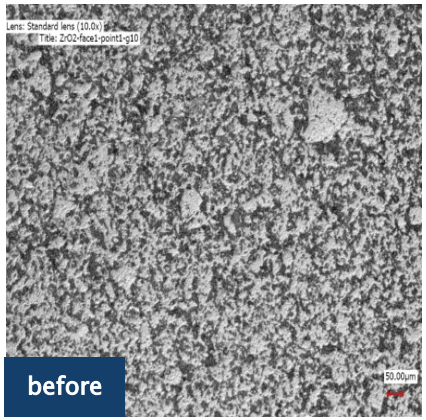
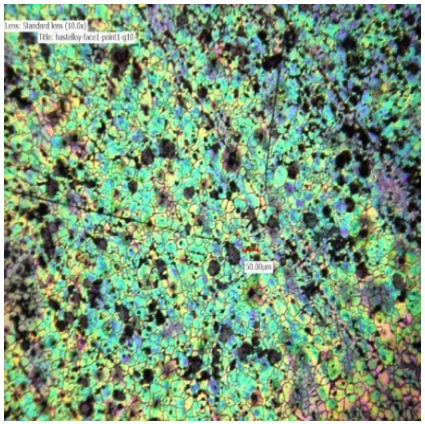
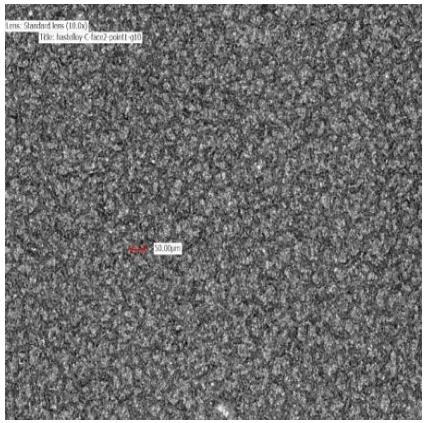
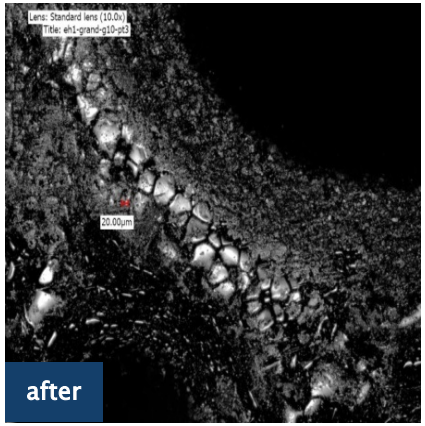
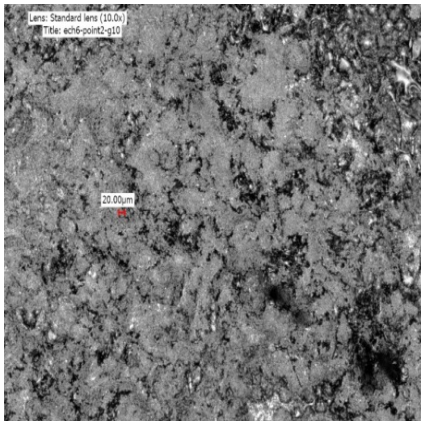
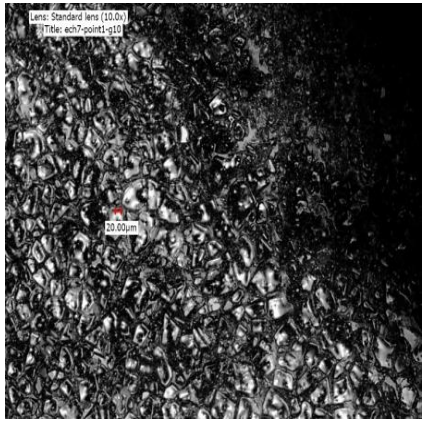
Confocal microscopy

ZrO_2 pellet	Hastelloy (ZrO_2 - 17 mol % Y_2O_3)	Hastelloy (ZrO_2 - 17 mol % Y_2O_3 + 10 mol % C)
 before		
 after		

ZrO_2 pellet

Before

- Homogenous surface

After

- Grains boundaries can be observed

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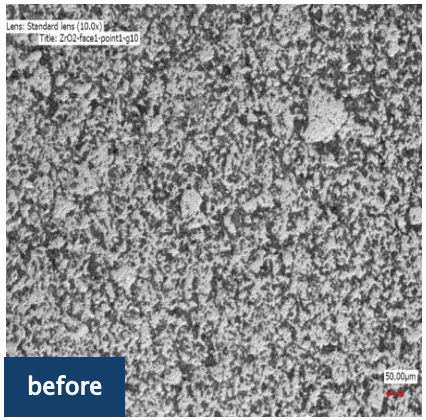
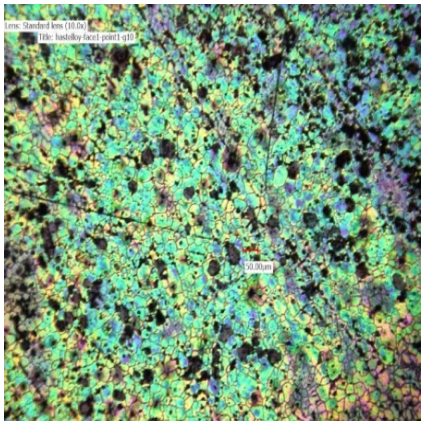
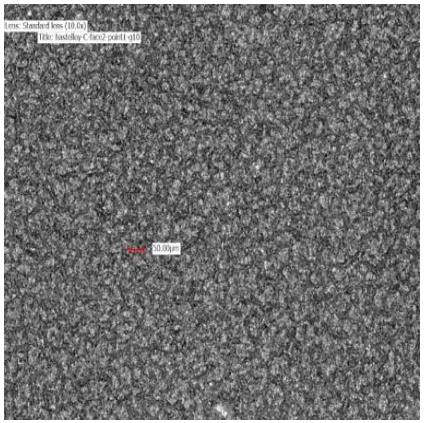
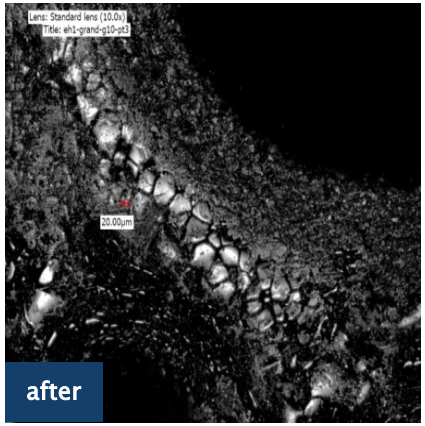
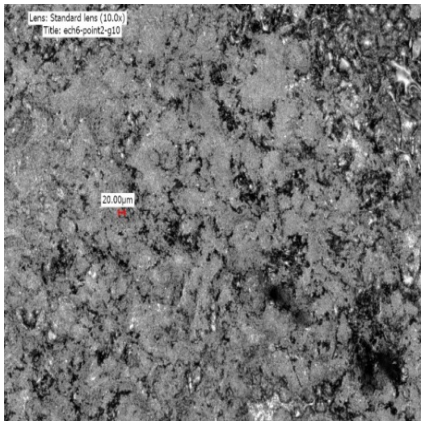
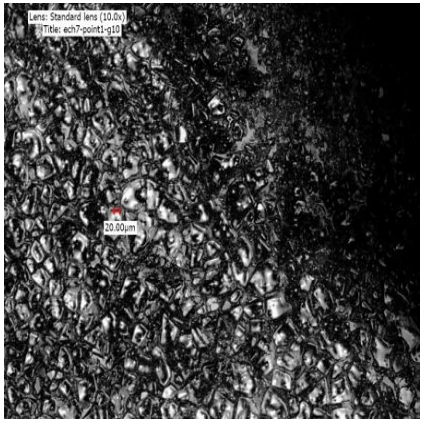
Confocal microscopy

ZrO_2 pellet	Hastelloy (ZrO_2 - 17 mol % Y_2O_3)	Hastelloy (ZrO_2 - 17 mol % Y_2O_3 + 10 mol % C)
 before		
 after		

Hastelloy substrats

Before

Coating: 17 % Y_2O_3

- Heterogeneous coating
- Grain boundaries and deposits with different aspects were observed

Coating: 17 % Y_2O_3 + 10 % C

- Homogeneous and regular coating

After

- Heterogeneous surface
- Degradation of Hastelloy coatings
- Increase of the roughness of the surface

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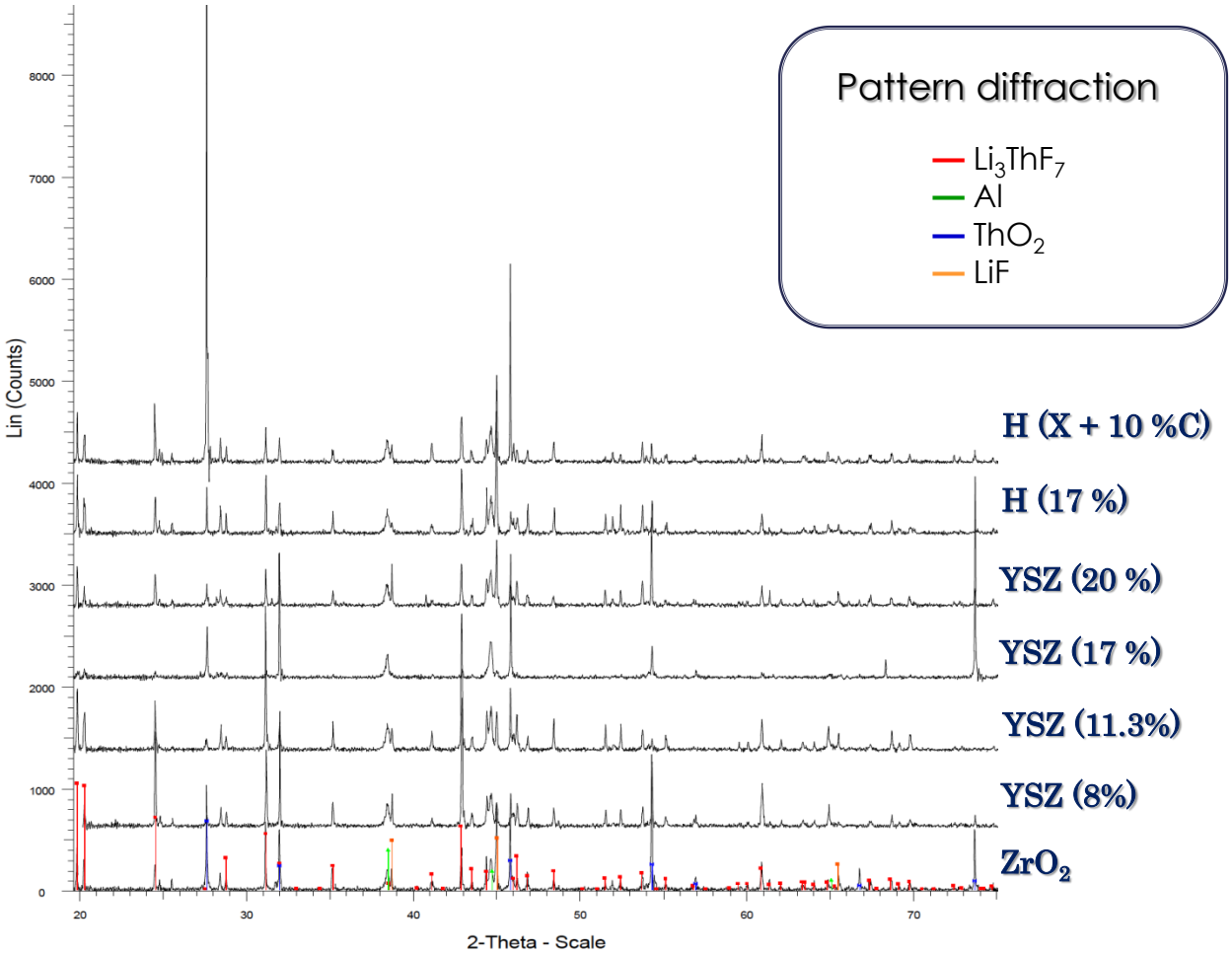
X-ray diffraction analysis – molten salt



- Chemical oxidation of Y_2O_3 in presence of THF_4 :

$$6ThF_4 + 4Y_2O_3 \rightarrow 6ThO_2 + 8YF_3$$

$\Delta G_{(750\ °C)}$ = -822,879 kJ

ICP analysis of the molten salt LiF-ThF_4

Pellets

YSZ	Zr (mmol/kg)	Y (mmol/kg)
ZrO_2	3	--
8 mol % Y_2O_3	4.3	1.4
11 mol % Y_2O_3	4.9	3.5
17 mol % Y_2O_3	2.7	0.8
20 mol % Y_2O_3	4.8	0.2

- Zr an Y were quantified (and also Th and Li)
- Low solubility of ZrO_2 in the molten salt
- Y concentration is more higher in molten salts with 8 - 11 mol % Y_2O_3 than the molten salts with 17 – 20 mol % Y_2O_3

Hastelloy substrate

Coating	Zr (mmol/kg)	Y (mmol/kg)	Ni (mmol/kg)	Mo (mmol/kg)
Y_2O_3	2.0	0.2	0.5	0.6
Y_2O_3 + C	2.3	0.3	3.4	17.8

- Ni, Mo, Y and Zr were quantified (and also Li and Th)
- The quantity of Y and Zr is the same in both molten salts and corresponds to the ratio initially present in the covered layer

Molten salt comparison:

- Molybdenum oxidation is more favorable in LiF-ThF_4

Coating comparison:

- C increases molybdenum corrosion

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Conclusion

- Degradation of all samples with a $t_{contact} \geq 15$ days

- All samples suffered a corrosion phenomenon as a result of the contact with LiF-ThF_4 molten salt at 750 °C.
  - Yttrium and zirconium were quantified in all molten salts (YSZ pellets and Hastelloy substrates)
  - Molybdenum and nickel were quantified in the molten salts containing the Hastelloy substrates .

- Hastelloy coatings are not stable in the LiF-ThF_4 then they are not protective against corrosion.

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Thank you for your attention