

Doping of ZrO₂ layer on ZIRLO for prevention of hydrogen pickup

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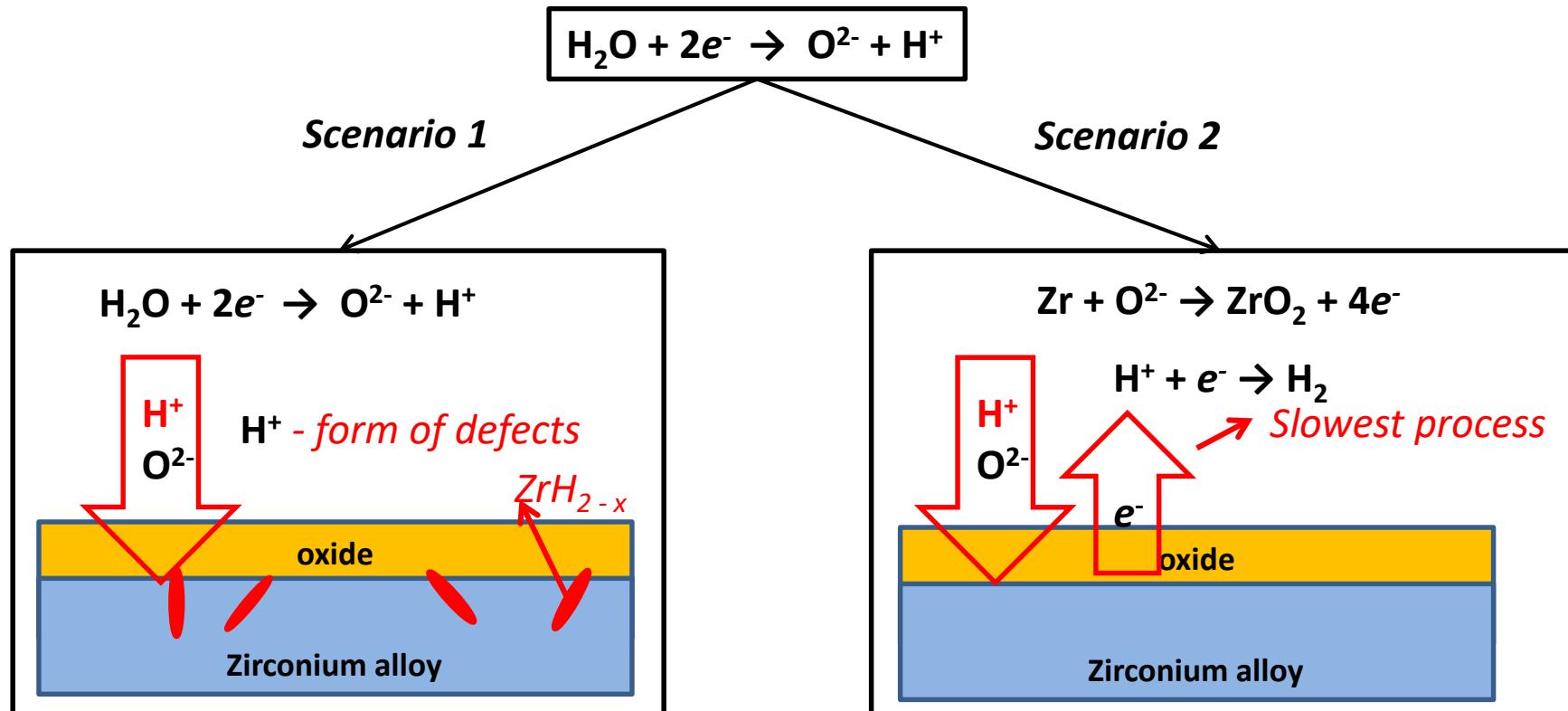


³ *AV Luikov Heat and Mass Transfer Institute, Minsk, Belarus*

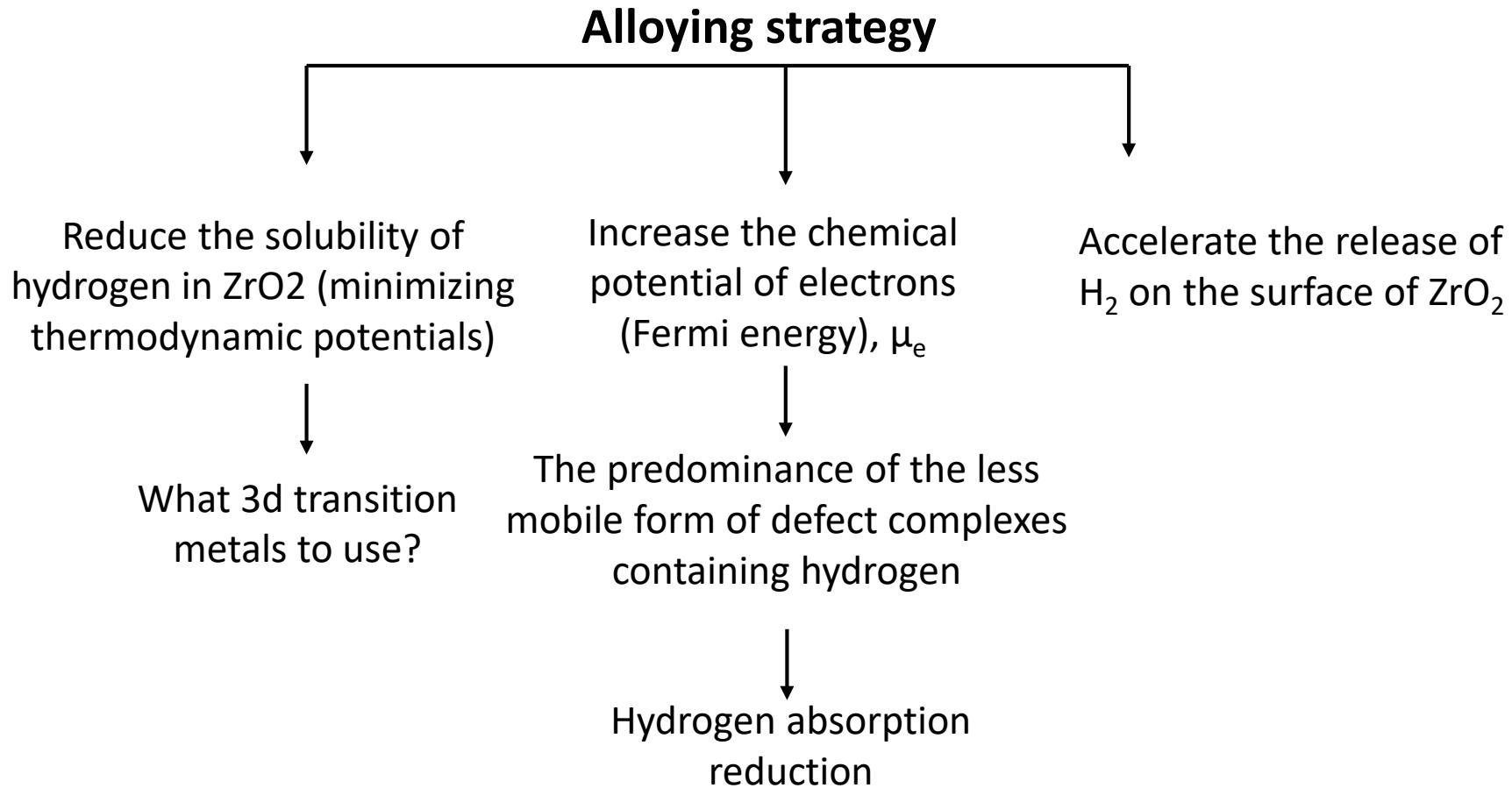


⁴ *Belarusian State University, Minsk, Belarus*

INTRODUCTION



Design of hydrogen resistant zirconium alloys



POTENTIAL ALLOYING ELEMENTS

| | |
|----------------------------------------|--------------------------------------------|
| 1 H Hydrogen 1.008 | 2 He Helium 4.003 |
| 3 Li Lithium 6.941 | 4 Be Beryllium 9.012 |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.305 |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 |
| 37 Rb Radium 84.468 | 38 Sr Strontium 87.62 |
| 55 Cs Cesium 132.905 | 39 Y Yttrium 88.906 |
| 87 Fr Francium 223.020 | 88 Ra Radium 226.025 |
| 89-103 Actinides | 104 Rf Rutherfordium [261] |
| | 105 Db Dubnium [262] |
| | 106 Sg Seaborgium [263] |
| | 107 Bh Bohrium [264] |
| | 108 Hs Hassium [265] |
| | 109 Mt Meitnerium [268] |
| | 110 Ds Darmstadtium [269] |
| | 111 Rg Roentgenium [272] |
| | 112 Cn Copernicium [277] |
| | 113 Nh Nhonium unknown |
| | 114 Fl Flerovium [289] |
| | 115 Mc Moscovium unknown |
| | 116 Lv Livermorium [298] |
| | 117 Ts Tennessee unknown |
| | 118 Og Oganesson unknown |

 Have a large thermal neutron capture cross section

 Impair the corrosive properties of zirconium

Part of the Zircaloy / ZIRLO



Increase zirconium hydrogenation

 Suitable for increasing the corrosion resistance of zirconium in reactor conditions

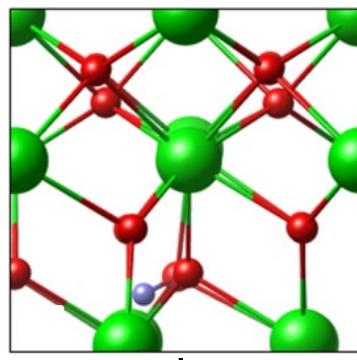


Increase chemical potential

Design of hydrogen resistant zirconium alloys (statistical thermodynamics and density functional theory *)

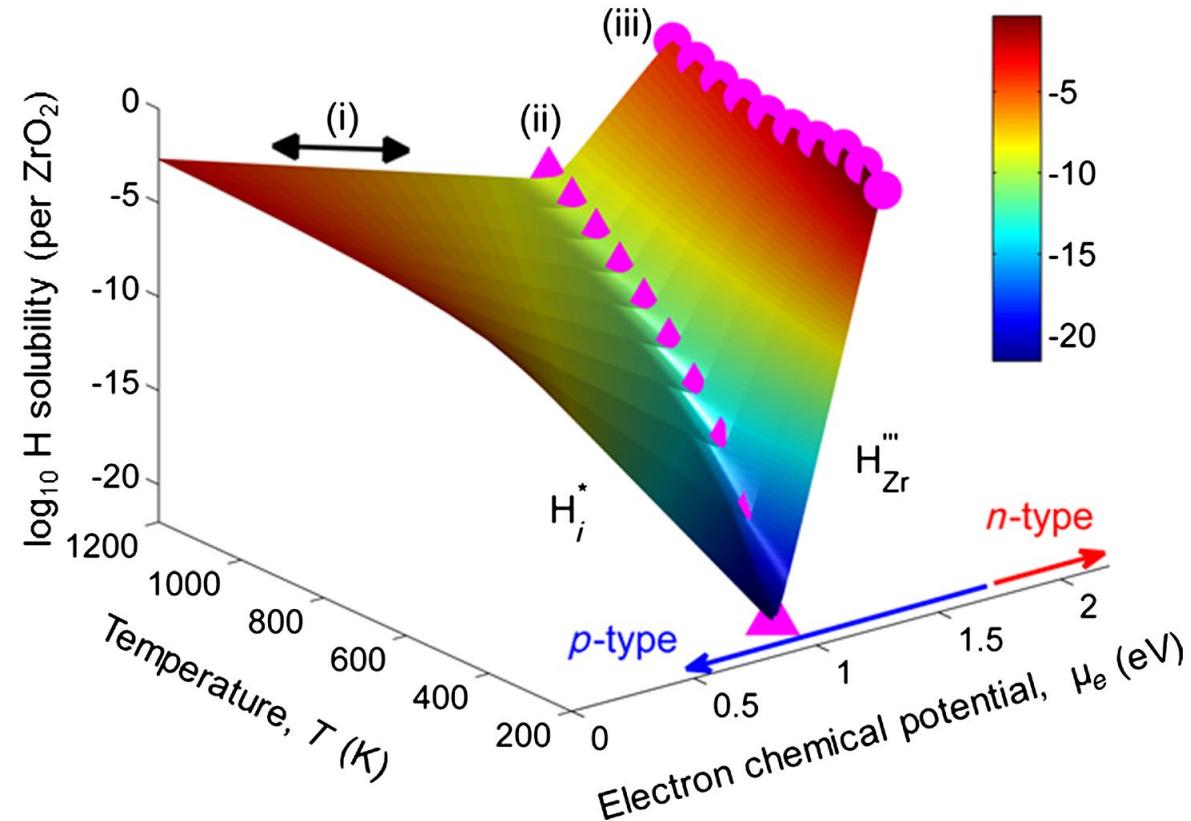
i – p-type alloying

Enhances solubility of hydrogen in ZrO_2 in the form of interstitial atom of hydrogen(H_i^*).



hydrogenation → zone (i)
undesirable

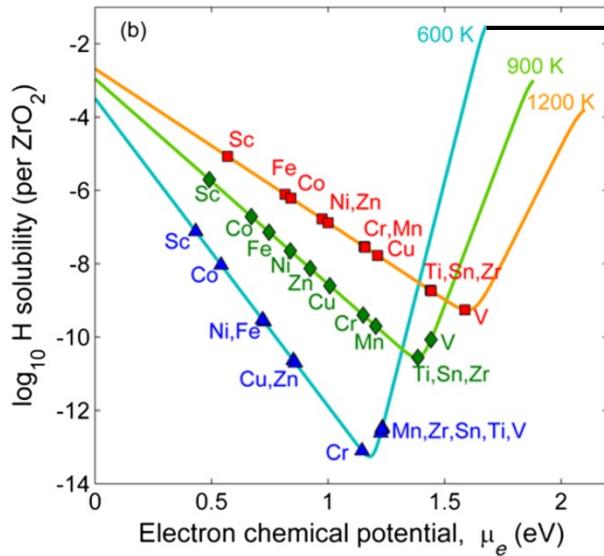
**Youssef,
Ying &
Yildiz
(2016)**



Recommendation: reducing of hydrogen solubility in ZrO_2 by alloying with elements that reduce the solubility of hydrogen.

Design of hydrogen resistant zirconium alloys

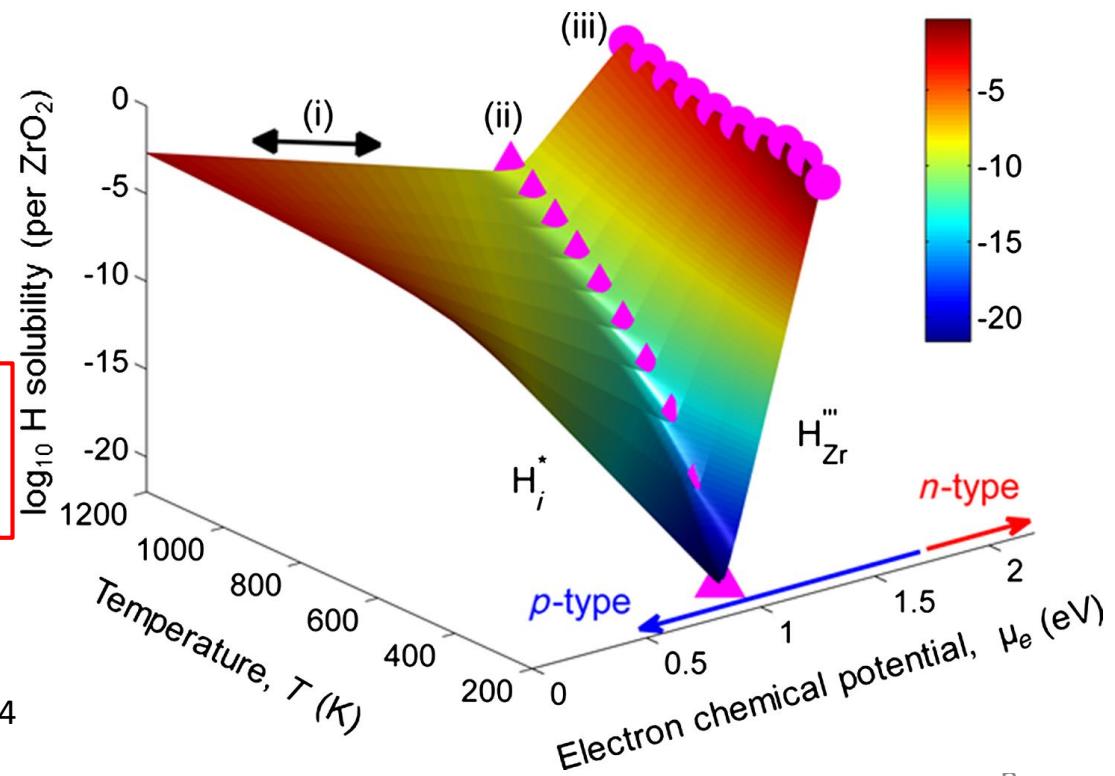
ii – alloying to reduce the solubility of hydrogen



Cr is the optimal alloying element for light water reactors(LWR).

Disadvantage :

Hydrogen absorption decrease of zirconium oxide is difficult due to the low μ_e (*p*-type alloying region) → penetration of a small amount of hydrogen into the zircaloy.



It is necessary to alloy the zirconium oxide with elements, which increase μ_e (*n*-type alloying region).

* M. Youssef et al. Physical Review Applied 5, 014

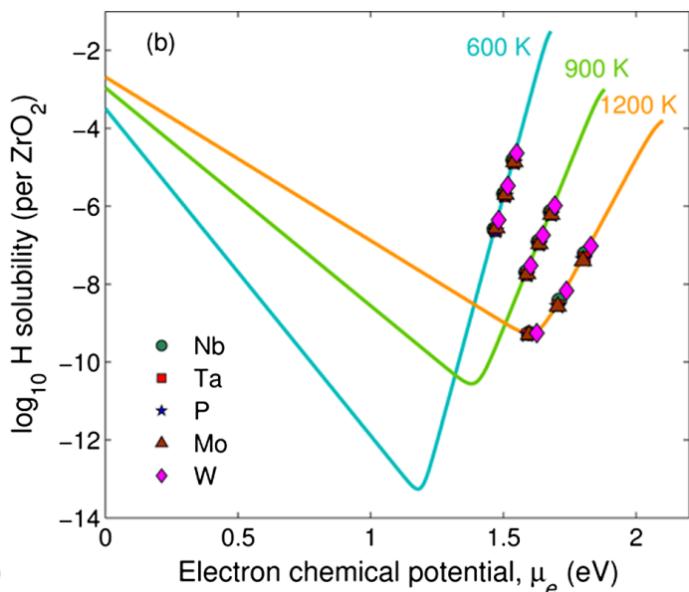
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Design of hydrogen resistant zirconium alloys

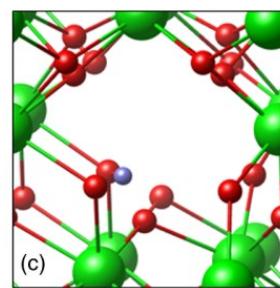
iii – alloying to increase μ_e

- The dissolution of hydrogen in m-ZrO₂ mainly in the form of complexes H_{Zr}^{'''} with limited mobility.

Nb, Ta, Mo, P and W increase μ_e when dissolved in m-ZrO₂.



Alloying increasing μ_e does not lead to increased corrosion processes in the zircaloy.

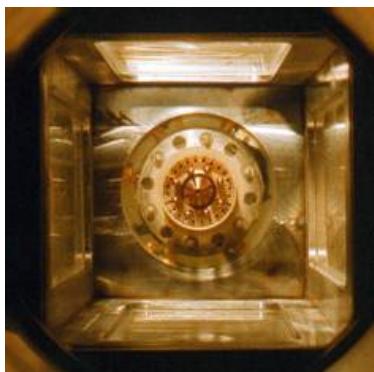
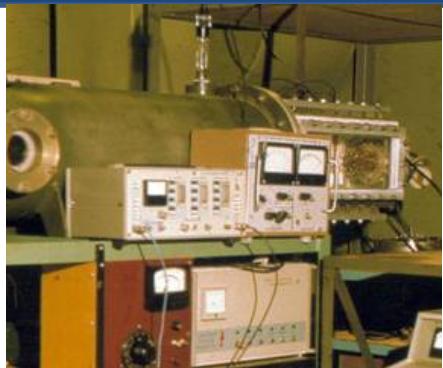


H_{Zr}^{'''}- Complex between single hydrogen and zirconium vacancy with charge state 3-

Chemical potential of electrons μ_e as a factor *, which can control the absorption of hydrogen in ZrO₂.

* M. Youssef et al. Physical Review Applied 5, 014008 (2016)

Magnetoplasma compressor with compact geometry



Experimental plant

Compression plasma flow

length — 10 – 12 cm

diameter — 1 – 2 cm

Plasma parameters:

Discharge time — 140 μ s

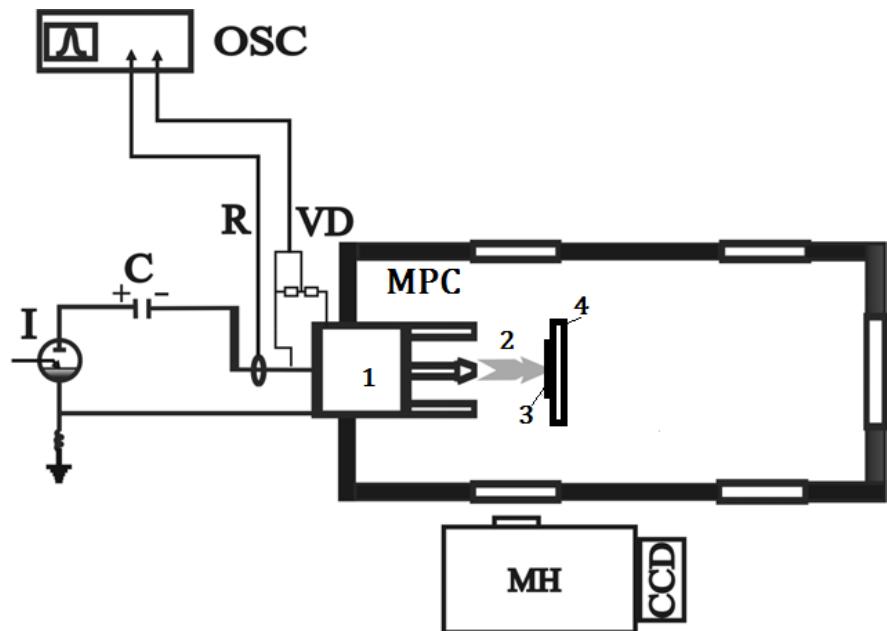
Maximum current — 50 ÷ 120 kA

Plasma speed — 30 ÷ 70 km/s

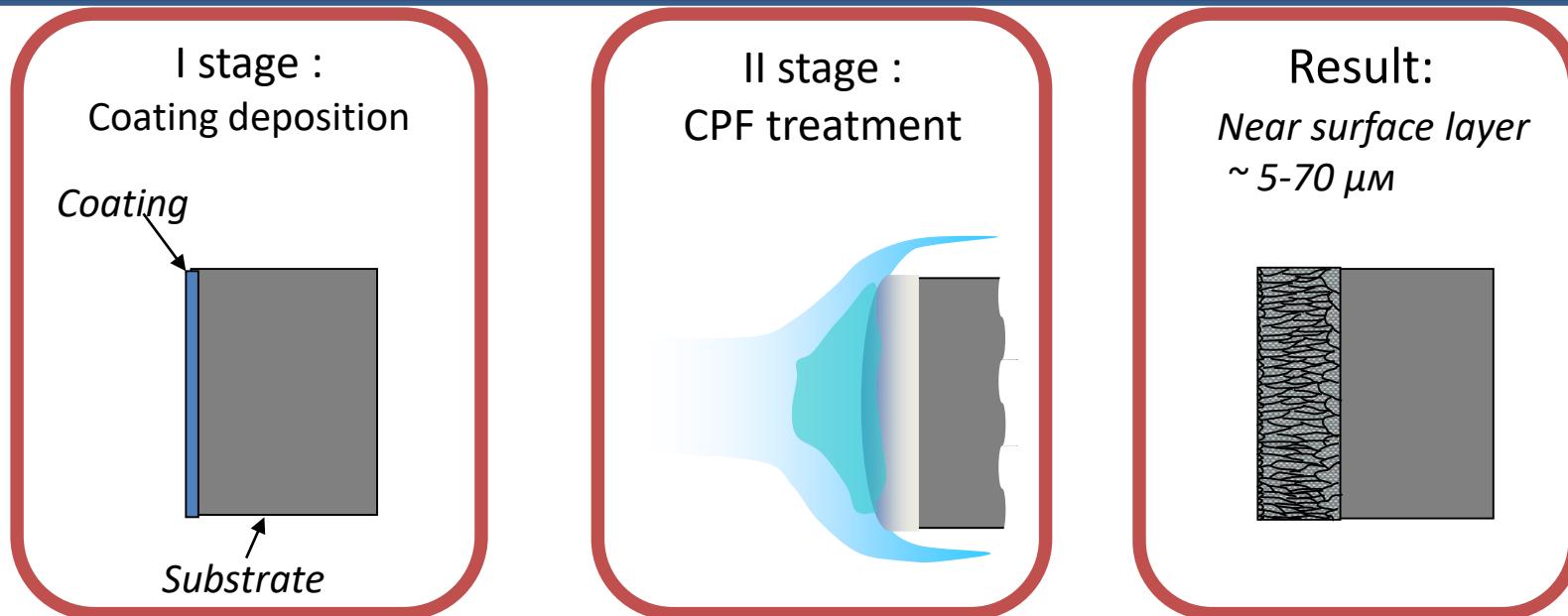
Electron density — $10^{16} \div 10^{18}$ cm⁻³

Plasma temperature — 2 ÷ 4 eV

Discharge device



PLASMA ALLOYING SCHEME



| Substrate | Alloying layer depth, μm |
|-----------|-------------------------------------|
| Fe | 5-20 |
| Al | 20-70 |
| Ti | 5-15 |

Alloying of materials by CPF allows to modify the mechanical properties, corrosion resistance, magnetic properties.

CHARACTERISATION

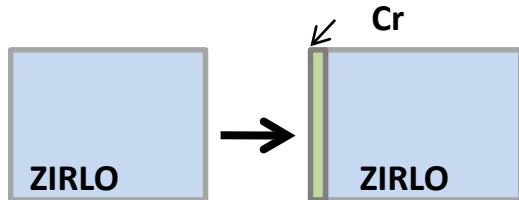
- 1. SEM → surface morphology → areas of interest**
- 2. FIB-SEM → extraction of TEM samples**
- 3. TEM → microstructural analysis**

EXPERIMENTAL



1 Stage

Cathodic arc deposition



- Coating thickness(1,0-1,5 µm)

Deposition parameters:

- arc current 100 – 180 A
- Bias voltage- 120 V

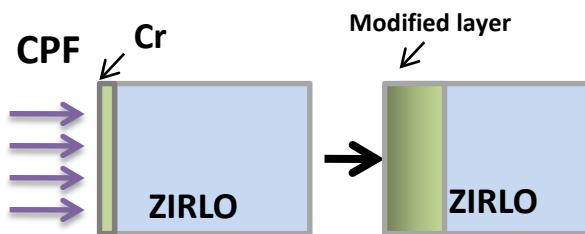


E-mail: ngongosamkelo@gmail.com



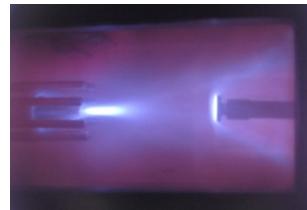
2 Stage

CPF treatment



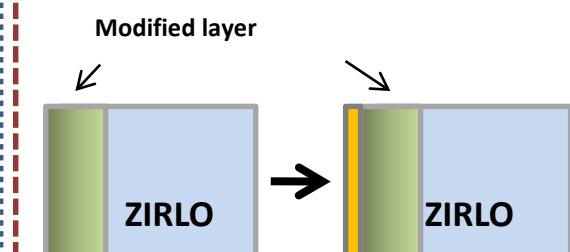
Plasma parameters:

- residual atmosphere: nitrogen N₂
- pressure: 400 Pa
- pulse duration : 100 µm
- *Number of pulses:* 3



3 Stage

Oxidation

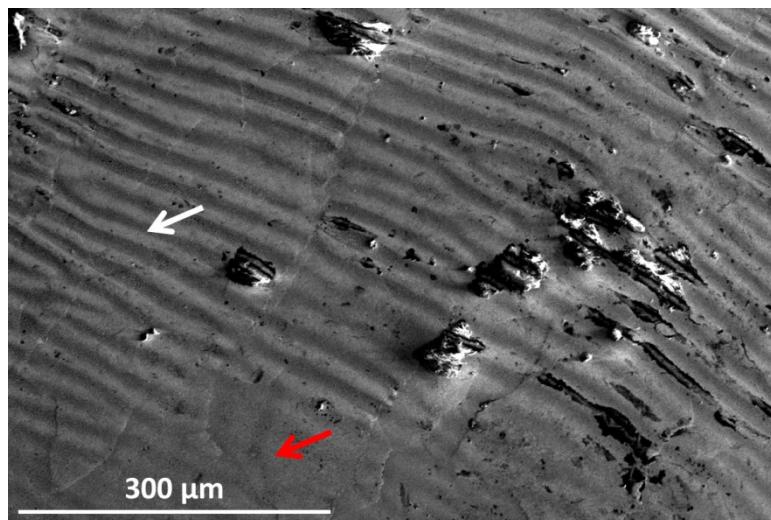


O₂

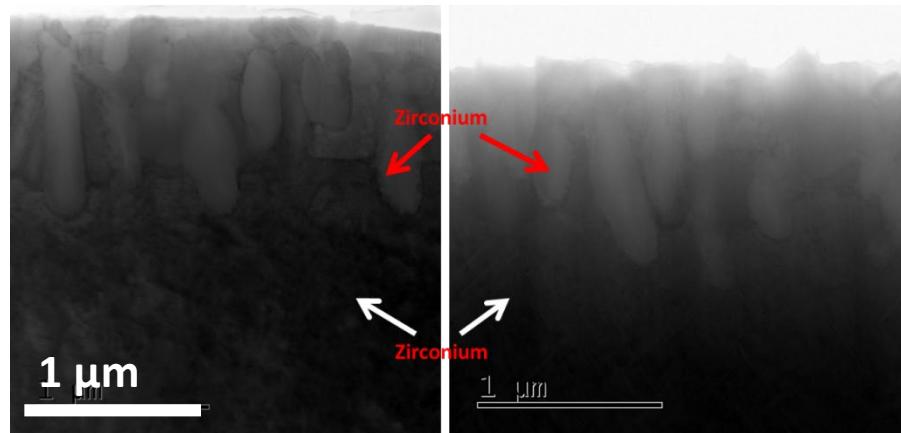
Oxidation parameters:

- 24 hours
- temperature 360 °C

ZIRLO/Cr → CPF



SEM surface morphology



BF-TEM cross - sectional

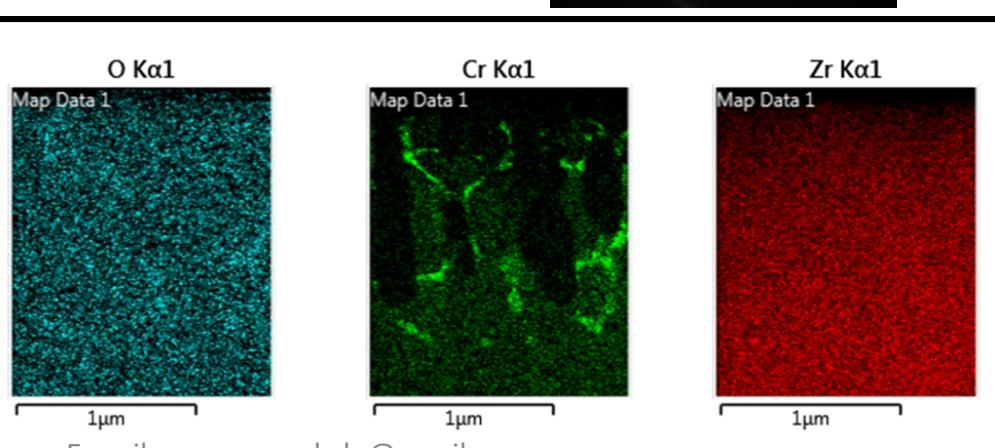
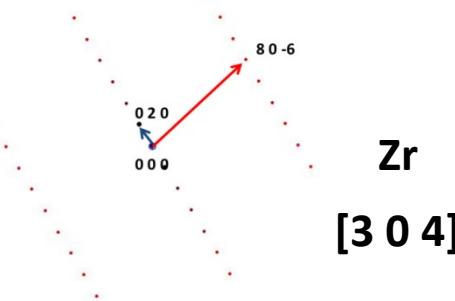
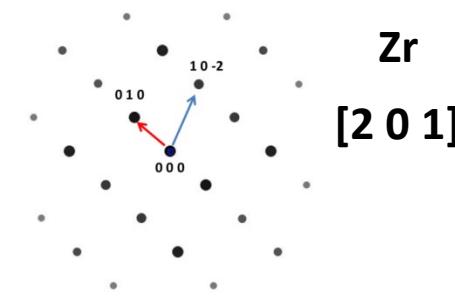
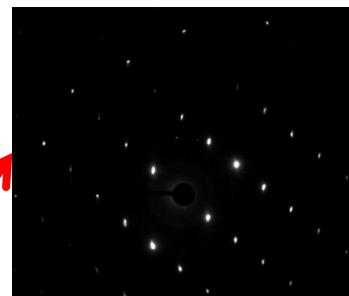
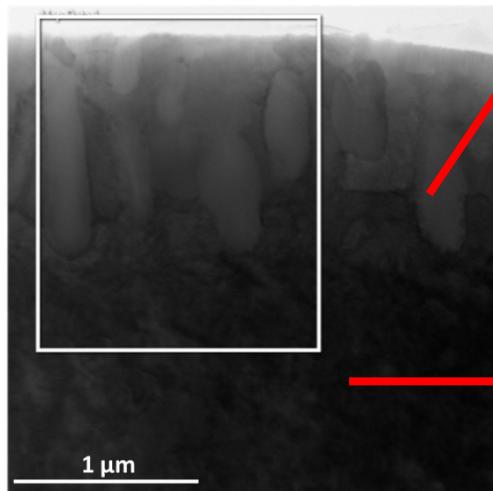
Plasma parameters:

- residual atmosphere: nitrogen N₂
- pressure: 400 Pa
- pulse duration : 100 μs
- *Number of pulses:* 3
($C_{Cr} = 2,3$ at.%)

- Ridges on the surface
- Formation of Zr columnar features
- Successful near surface modification with ~ 1 μm

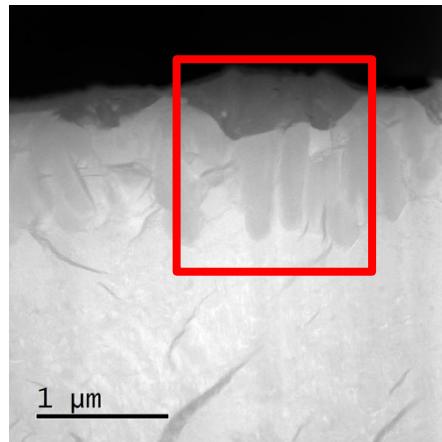
ZIRLO/Cr → CPF

BF-TEM image of a modified sample



- Cr at the grains boundaries
- As an alloying element Cr tends to occupy grain boundaries
-

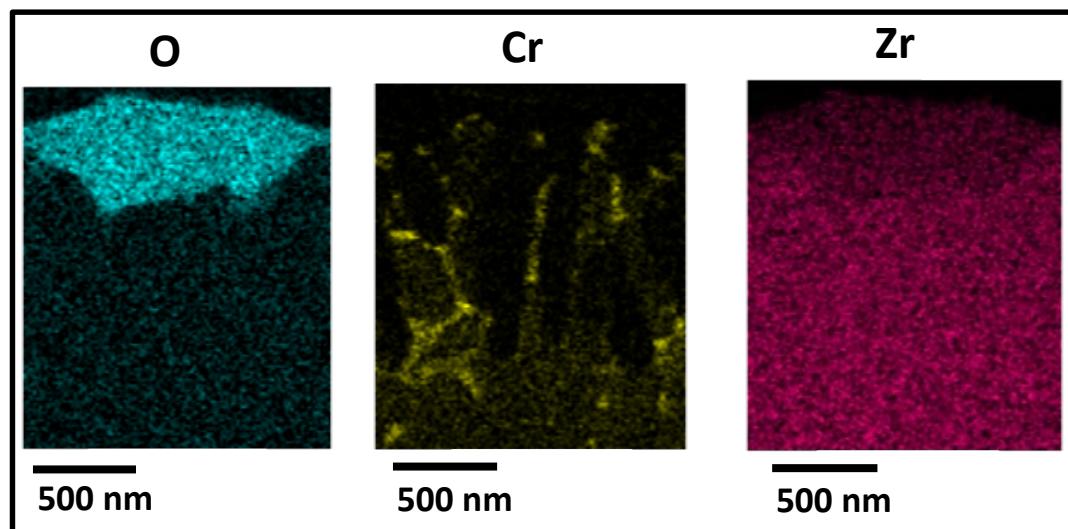
ZIRLO/Cr → CPF → Oxidised



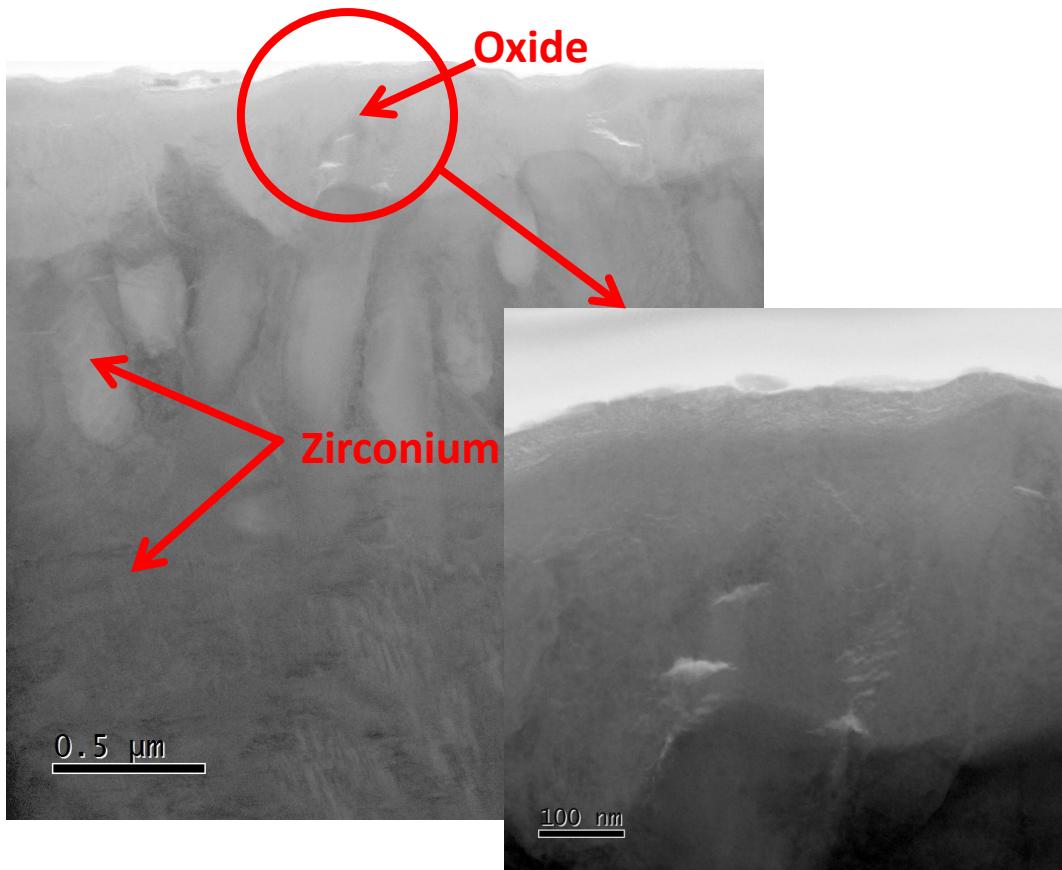
Annealing in oxygen atmosphere for 24 hours at 360°C

- Cr at the grains boundaries
- Formation of nodular oxide layer
- Cr is present in zirconium oxide.

TEM EDS cross section

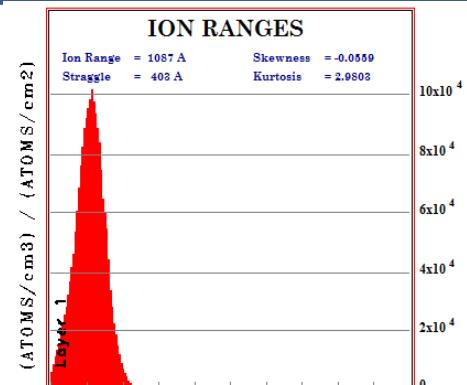


ZIRLO/Cr → CPF → Oxidised → H⁺

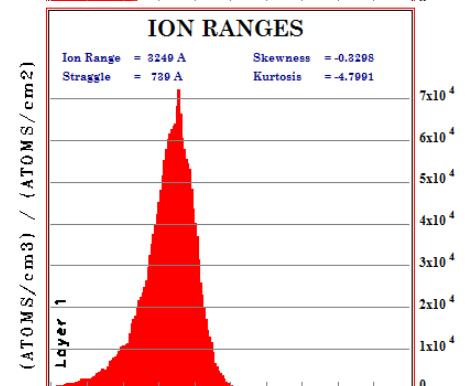


SRIM calculations

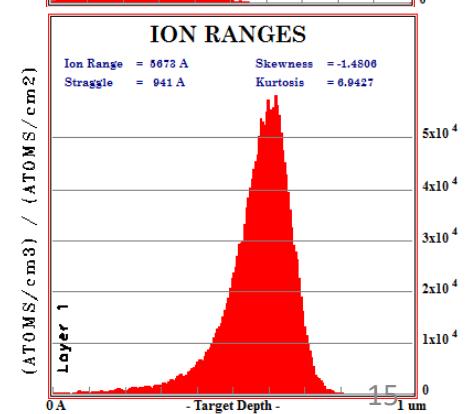
12.5 keV
100 nm



50 keV
0.35 μm



97.5 keV
0.60 μm

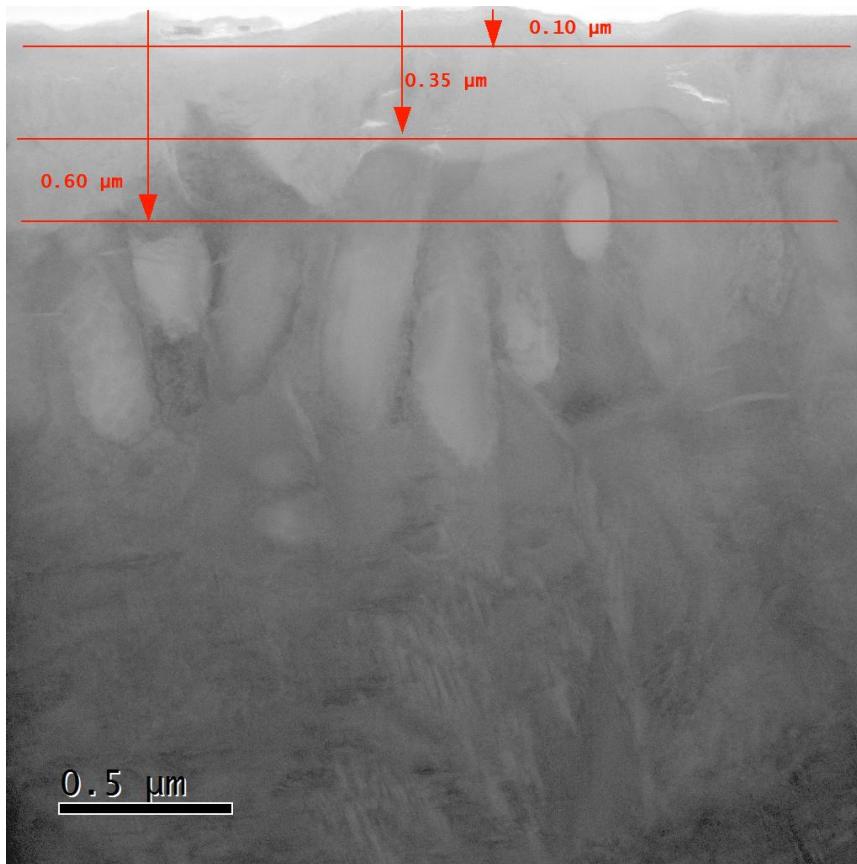


BF TEM cross sectional images

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HYDROGEN DESORPTION

SRIM calculations



Hydrogen pick up investigation was carried out on a special Gas Reaction Controller complex

Hydrogen saturation parameters:

- Temperature: 360 °C
- Hydrogen pressure: 2 atm
- Time: 2 hours

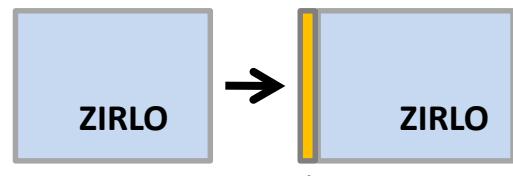
Hydrogen desorption

| Sample | Hydrogen desorption rate, 10^{-4} mass%/min |
|--------------|-----------------------------------------------|
| ZIRLO | 24 |
| CPF:ZIRLO | 23.5 |
| CPF:Cr/ZIRLO | 8.4 |

EXPERIMENTAL



1 Stage Oxidation



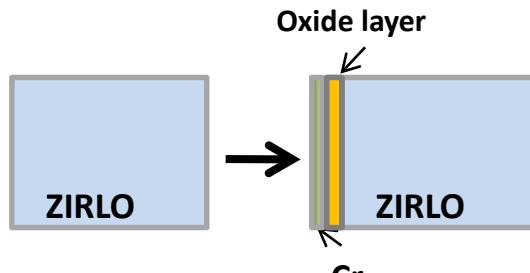
O₂

Oxidation parameters:

- 24 hours
- temperature 360 °C



2 Stage Cathodic arc deposition



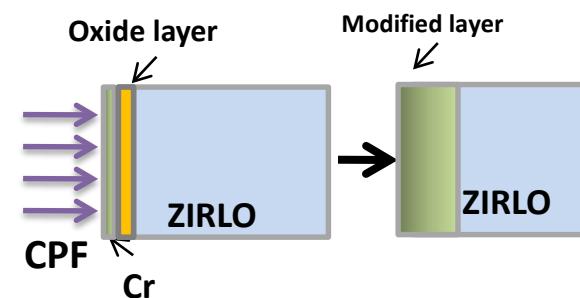
- Coating thickness(1,0-1,5 µm)

Deposition parameters:

- arc current 100 – 180 A
- Bias voltage- 120 V

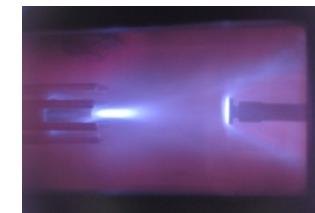


3 Stage CPF treatment



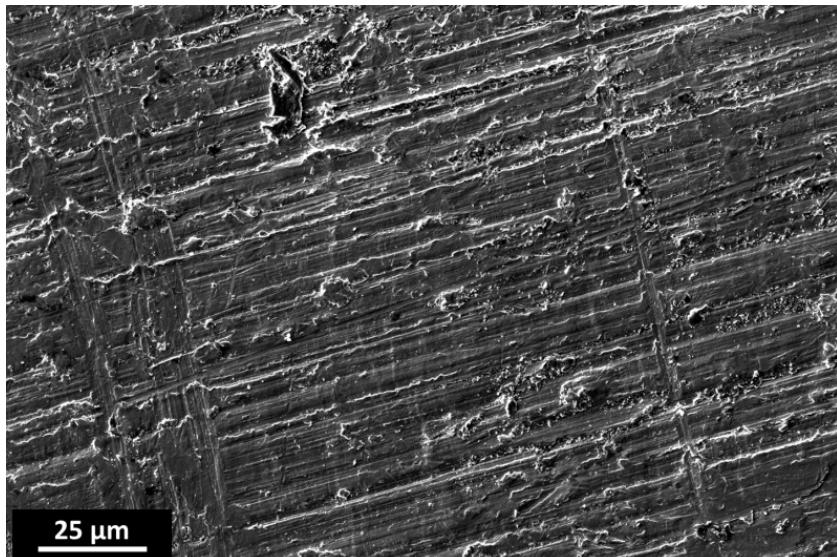
Plasma parameters:

- residual atmosphere: nitrogen N₂
- pressure: 400 Pa
- pulse duration : 100 µm
- *Number of pulses:* 3



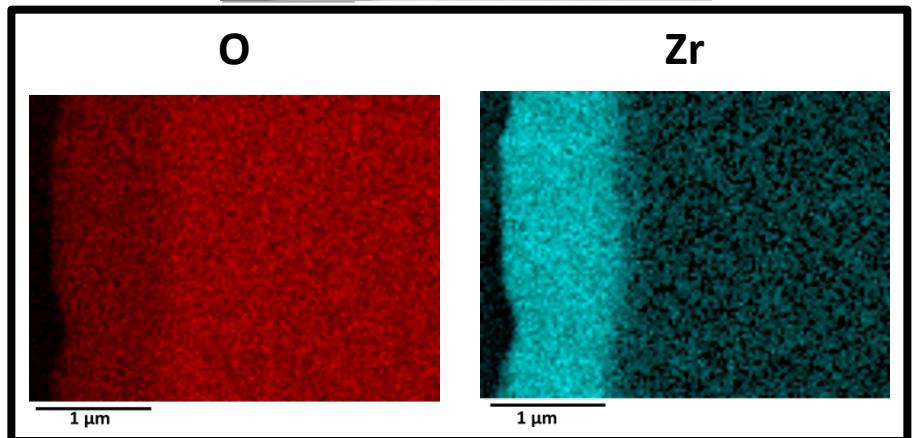
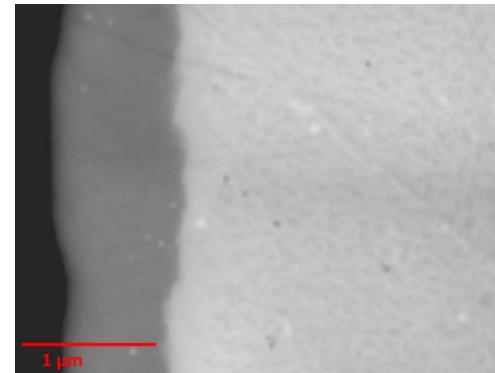
ZIRLO → Oxidised

SEM surface morphology



- Formation of uniform oxide layer
- Oxide thickness of $\sim 1 \mu\text{m}$

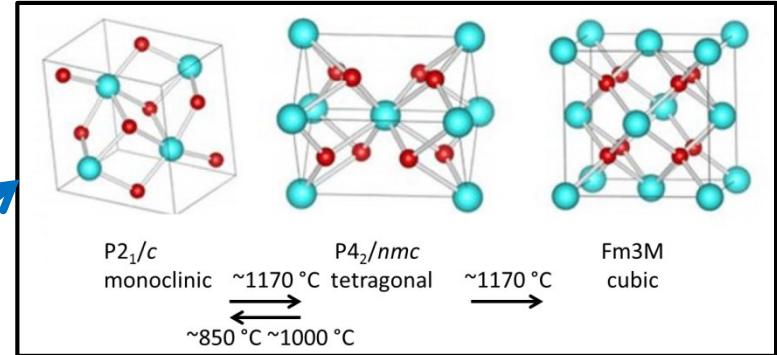
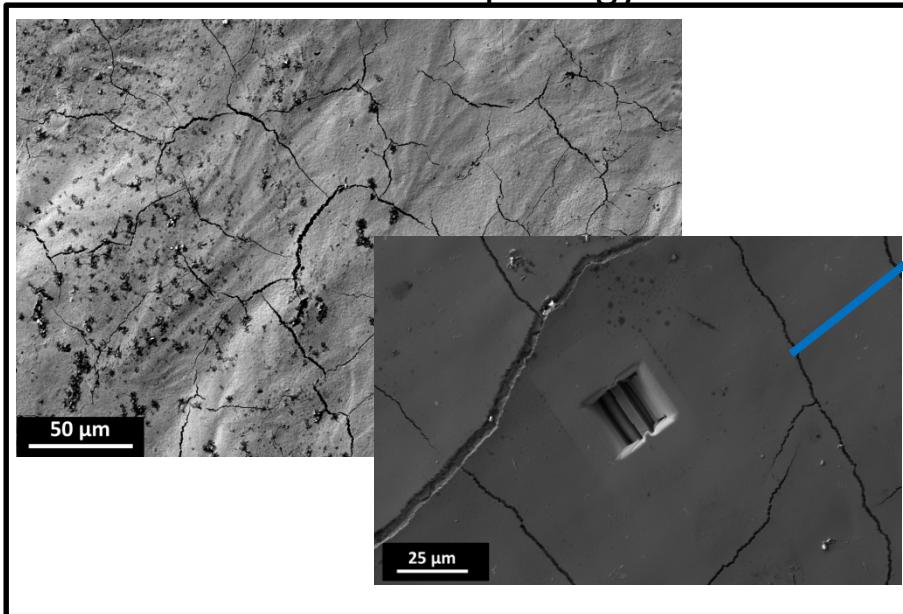
SEM image of the cross section



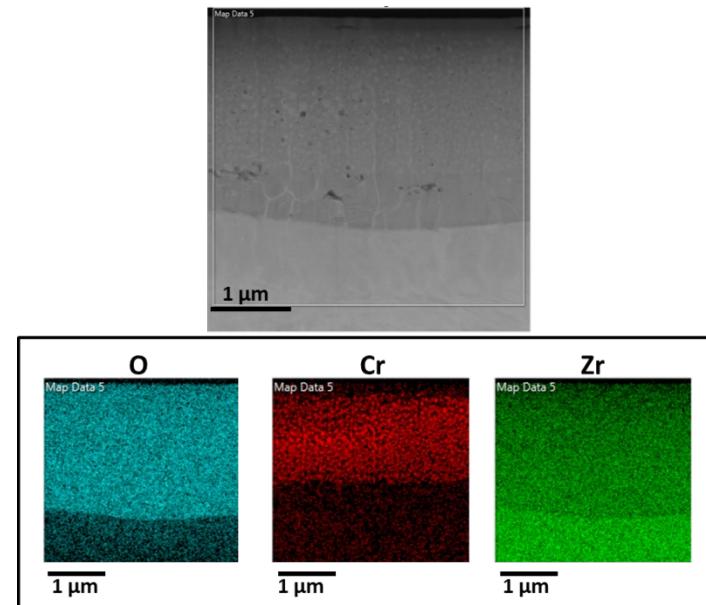
SEM EDS results

ZIRLO → Oxidised → Cr → CPF

SEM surface morphology



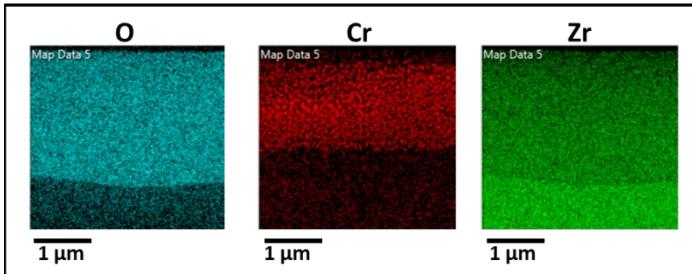
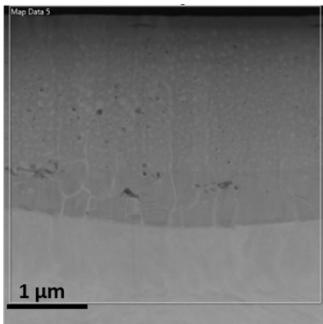
TEM image of the cross-section



TEM EDS results

ZIRLO → Oxidised → Cr → CPF → H⁺

TEM image of the cross section



TEM EDS results

| Sample | Hydrogen desorption rate, 10 ⁻⁴ mass%/min |
|--------------|------------------------------------------------------|
| ZIRLO | 24 |
| CPF:ZIRLO | 23.5 |
| CPF:Cr/ZIRLO | 8.4 |

Irradiation energies



Hydrogen saturation parameters:

- Temperature: 360 °C
- Hydrogen pressure: 2 atm
- Time: 2 hours

Hydrogen desorption

| Sample | Hydrogen desorption rate, 10 ⁻⁴ mass%/min |
|----------------------------|------------------------------------------------------|
| Pre-oxidised ZIRLO | 2 |
| CPF: pre-oxidised ZIRLO | 1.8 |
| CPF: Cr/pre-oxidised ZIRLO | 0.9 |

CONCLUSION & FUTURE WORK

1. Surface modification with CPF was successful with $\sim 2 \mu\text{m}$ of oxide layer with chromium
2. The downside was crack formation on the surface of the material
3. Hydrogen desorption was reduced by ~ 2 times to the normal ZIRLO with an oxide layer.
4. The next step is to find a way to prevent the crack formation on the surface of the ZIRLO.

ACKNOWLEDGEMENTS

Prof Neethling and Dr Janse van Vuuren my supervisors

DST, NRF and NMMU for financial support

Westinghouse Electric Company LLC and CARAT for providing the ZIRLO® for the experiments

Prof Uglov for modification of ZIRLO surface

CHRTEM for research techniques