DE LA RECHERCHE À L'INDUSTRIE

CEA studies on nuclear fuel claddings for LWRs enhanced accident tolerant fuel: recent results, pending issues and prospects

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+ collaboration with partners from french universities

OECD-NEA Meeting on Increased Accident Tolerance of Fuels for LWRs, Issy-les-Moulineaux, France, Oct. 28-29, 2013

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References:

[1] M. Le Flem, et al., "Evaluation of potential alternative nuclear fuel cladding materials for LWRs – CEA studies", proceeding of OECD-NEA ATF Workshop, Dec. 10th, 2012, Issy-les-Moulineaux, France

[2] I. Idarraga et al., "Assessment at CEA of coated nuclear fuel cladding for LWRs with increased margins in LOCA and beyond LOCA conditions", proceeding of 2013 LWR Fuel Performance Meeting/TopFuel, Charlotte, USA, Sept. 15-19, 2013

[3] C. Sauder et al., '"Assessment of SiC/SiC cladding for LWRs", proceeding of 2013 LWR Fuel Performance Meeting/TopFuel, Charlotte, USA, Sept. 15-19, 2013

INTRODUCTION

Some targets for new claddings to sustain LOCA (and beyond) transient:

→ Decrease oxidation rate with steam water at high temperature

→ Improve the mechanical properties at high temperature

- *Lowering deformation level to keep coolability or the core (flow blockage)*

→ Increase the margin to melting

Prospective studies on enhanced accident tolerant fuel/cladding at CEA

1- Coated Zr clad

2- SiC/SiC + liner composites

→ *C. Sauder, A. Michaux et al. (CEA),*
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Assess the advantages in terms of performance towards LOCA and beyond and check the good in-service behavior

Specific targets for optimized coating on Zr base claddings:

Decrease the HT oxidation rate with steam water:

→ **to slow down/delay the gaseous hydrogen release** (mitigation of explosion risk)

→ **to increase the HT oxidation time/temperature margin vs. quenching and post-quenching embrittlement limit** (avoid multi-fragmentation…)

→ ***potential positive effect on PCT*** *by reducing the contribution of the heat of the HT oxidation exothermic reaction on the cladding temperature incursion => has to be quantified*

Points not specifically addressed by such clad concept:

→ *Impact on HT mechanical properties => has to be quantified*

→ *No increase of the margin to melting => Eutectic formation between Zr and Cr at ~1330℃*

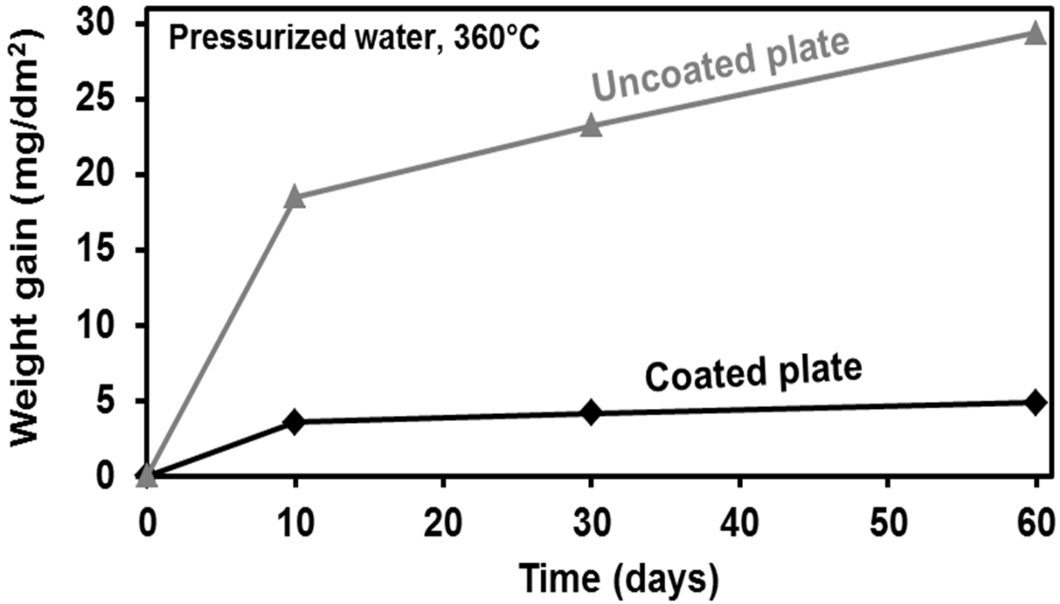
- Having an iterative solution involving thin coatings on well-known Zr cladding materials
  - No significant change in fuel sub-assembly geometry, mechanical / thermal properties…
  - Potential use of penalizing elements (in terms of neutron compatibility)…

Main challenges:

- Find the appropriate composition of the coating
- Fabricate an homogeneous coating with suitable process
- Keep the coating efficiency for in-service conditions => effects of neutron irradiation ?
- Avoid early spalling of the coating at high temperature, industrial issues, etc…

- <u>More than 20 coatings </u>(including ceramics, and metals) were investigated at CEA these last 7 years
- Among all, optimized Cr base-coatings have shown encouraging behavior

→ **<u>Significant decrease in the oxidation kinetics for both in-service (out-of-pile) conditions and at high temperature (1000-1200℃) typical of LOCA</u>**

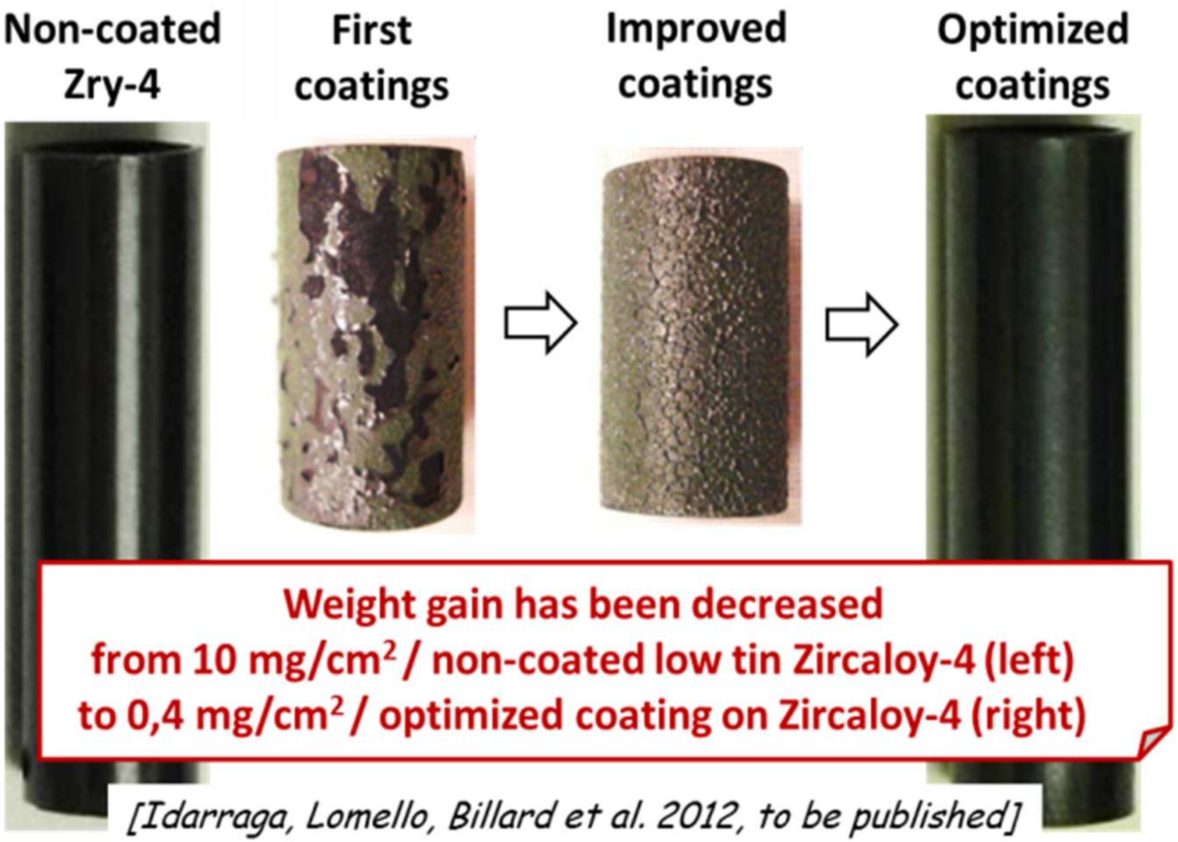


<u>Oxidation at 360℃, 60 days, pressurized water at 190 b ar, relevant PWR chemistry</u>

TRANSPOSITION OF THE COATING PROCESS TO TUBULAR GEOMETRY

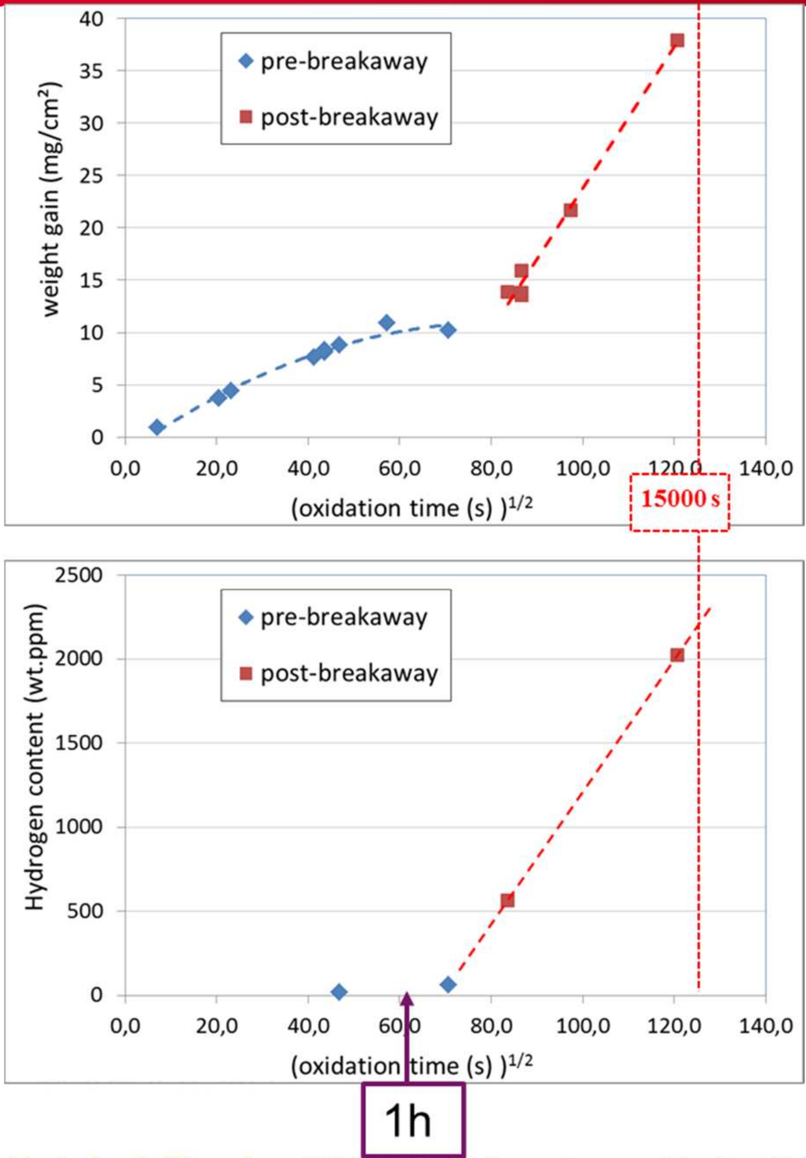
1- Coated Zr clad

- Experiments performed on the most promising coatings obtained previously on flat specimens
- Weight gain, µstructural observations/analysis, Post-quench mechanical tests…
- **Illustration of the results obtained after steam oxidation at 1200°C for 300 s:**



RECENT RESULTS FOR "SLIGHTLY BEYOND LOCA" CONDITIONS ("BREAKAWAY"… ~4 HOURS AT 1000℃)

1- Coated Zr clad



Behavior of uncoated Zirc-4:

Two side oxidation performed in a steam environment at 1000℃ (DEZIROX facility), followed by water quenching from the oxidation temperature down to RT

The onset of post breakaway regime (~5000s) is linked to the beginning of hydrogen pick up

➔ **after 15000s (>4h)** at 1000℃, **high embrittlement of uncoated Zy-4** due to the **high hydrogen uptake (~2000-3000 wt.ppm)**

Ref. : L. Portier et al., Journal of ASTM International, February 2005, Vol. 2, No. 2 Paper ID JAI12468

OXIDATION OF COATED/NON COATED ZY-4 AFTER 15000S AT 1000℃

1- Coated Zr clad

	un-coated Zry-4	Non optimized coating	Optimized coating
Weight gain (mg/cm^2)	37-40	11.2	**2.5**
Zirconia thickness (µm)	~250	0	**0**
α_{Zr}(O)	~100µm	<100µm + α_{Zr}(O) incursions	**0µm + very few α_{Zr}(O) incursions**
Hydrogen content (wt.ppm)	**~2000-3000**	**~1000**	**≤80**

For the uncoated Zry-4, the weight gain and the associated hydrogen pick-up are fully consistent with the previous results obtained on low-tin Zry-4 cladding tubes

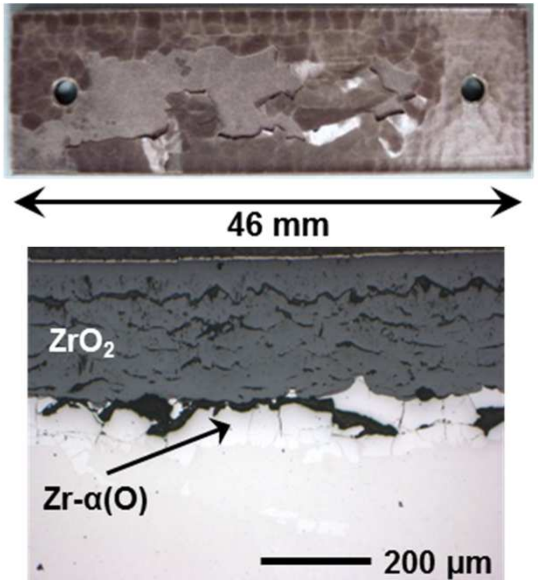
The non-optimized coating induces an intermediate behavior with no significant oxide formation but with some evidence of α_{Zr}(O) incursions into the Zry-4 metallic (prior-β_{Zr}) substrate and an associated significant hydrogen pick-up

The optimized coating exhibits a very good resistance to both oxidation and hydrogen up-take:

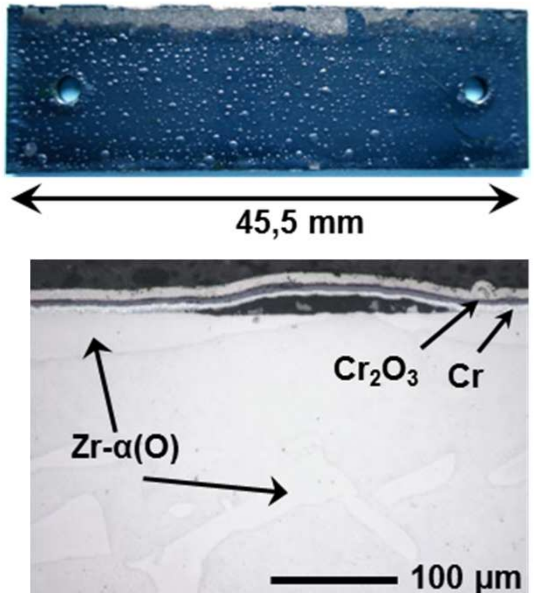
(i) absence of significant zirconia formation nor oxygen diffusion into the metallic prior-β_{Zr} substrate

(ii) no significant hydrogen pick-up (<80 wt.ppm).

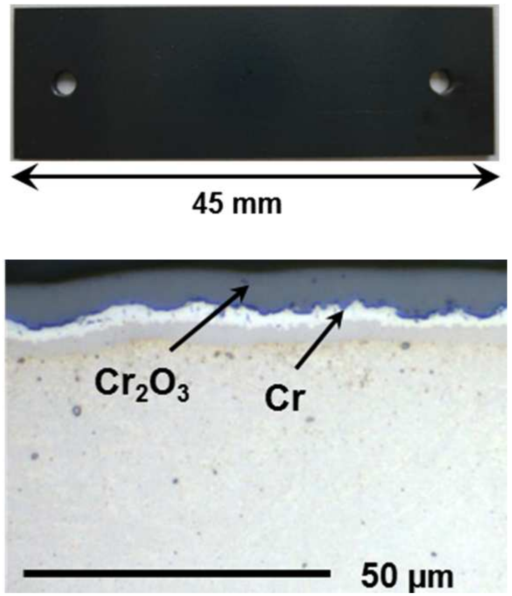
OPTICAL MACRO/MICROGRAPHS OF UNCOATED/COATED ZIRC-4 AFTER STEAM OXIDATION FOR 15000 S @ 1000°C



Uncoated Zy-4



Non optimized coating



Optimized coating

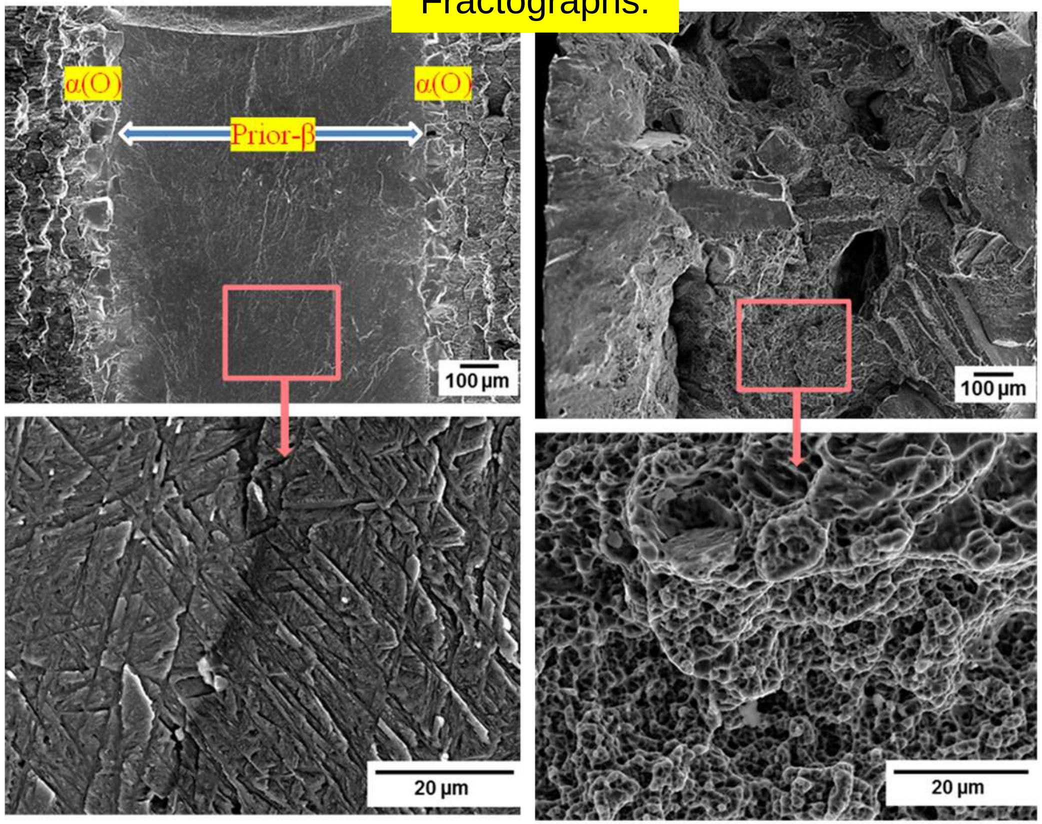
POST-OXIDATION (15000 S @1000℃) MECHANICAL TENSILE PROPERTIES

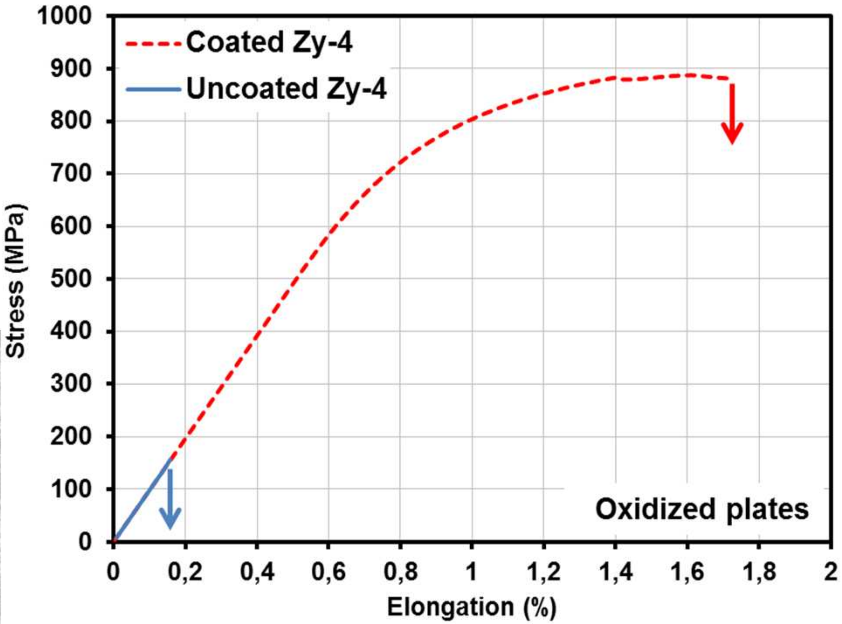
1- Coated Zr clad

Engineering tensile stress-strain curves obtained at RT on uncoated and optimized coated Zry-4 (after two-side steam oxidation for 15000 s at 1000℃)

Uncoated: Coated:

Fractographs:





Uncoated Zry-4:
- no significant necking,
- full brittle failure mode

Optimized coated Zry-4:
- significant necking,
- ductile failure mode (mid-clad-thickness)

CONCLUSIONS AND FURTHER WORK

Status of the R&D on innovative coated Zr cladding for PWR at CEA

- Optimized of Cr base coatings on Zy-4 gave encouraging results so far
  - Decrease in weight gain in nominal, LOCA and slightly beyond LOCA conditions
  - Post-quench ductility is enhanced by avoiding ZrO_2 and Zrα(O) and reducing the oxygen content in the beta layer
  - Promising results on hydrogen pick up (no Breakaway phenomena)
- Homogeneous coating on Zy-4 clad segment has been achieved (~10 cm in length)

Further work, pending issues

- Optimisation of Cr-base coatings on longer cladding tubes, & test the behavior at higher oxidation temperatures (up to 1300-1400°C, Zr-Cr eute ctic formation consequences ?) & for higher oxidation times, i.e., for more « beyond LOCA » conditions…
- Assessment of those coatings in other relevant nominal and accidental scenarios, including under neutron irradiation (*)
- Assessment of the potential margins achieved by relevant LOCA transients calculations (adapt existing codes and methodology) (*)

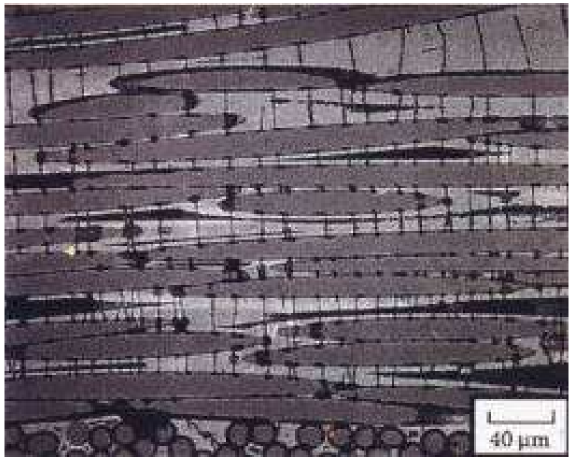
(*) *Topics where international collaboration could be of interest…*

INTRODUCTION

2- SiC/SiC + liner composites

Purpose

- Enhance oxidation resistance (thermodynamics, kinetics)
- Increase margin to fusion (decomposition temperature > 2000°C)
- Providing a stiff and resistant cladding
  - o in order to keep a « coolable » core
  - o to avoid fuel relocalization
  - o and to keep the fuel confinment



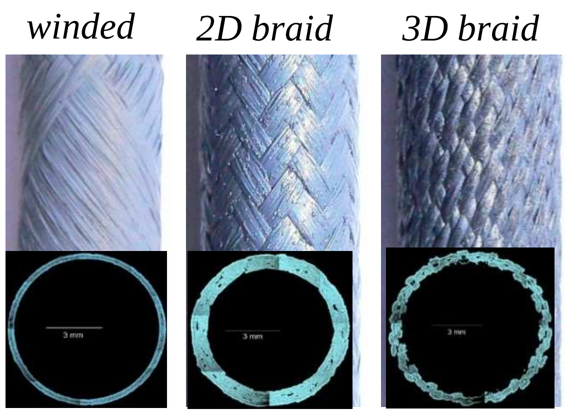
Matrix multi-cracking

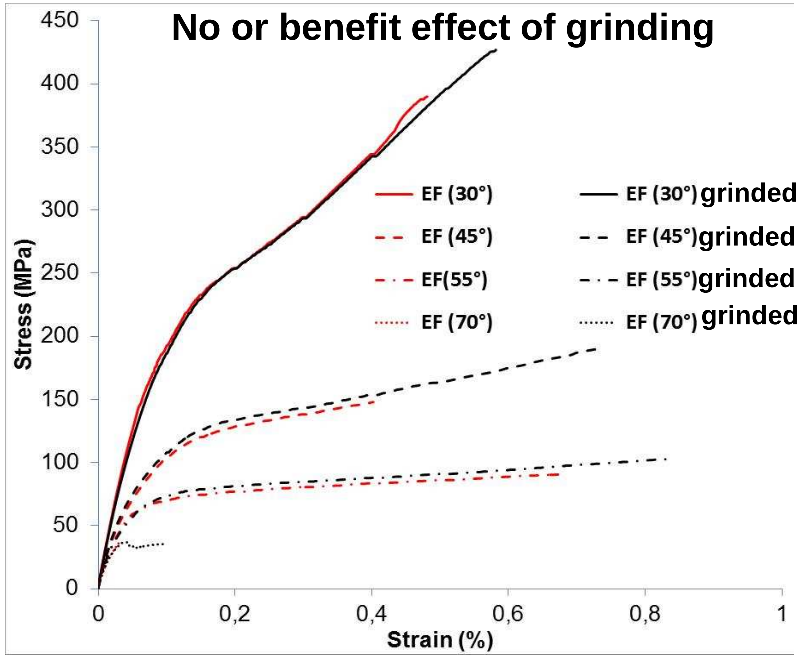
Main challenges of SiC/SiC for PWR cladding

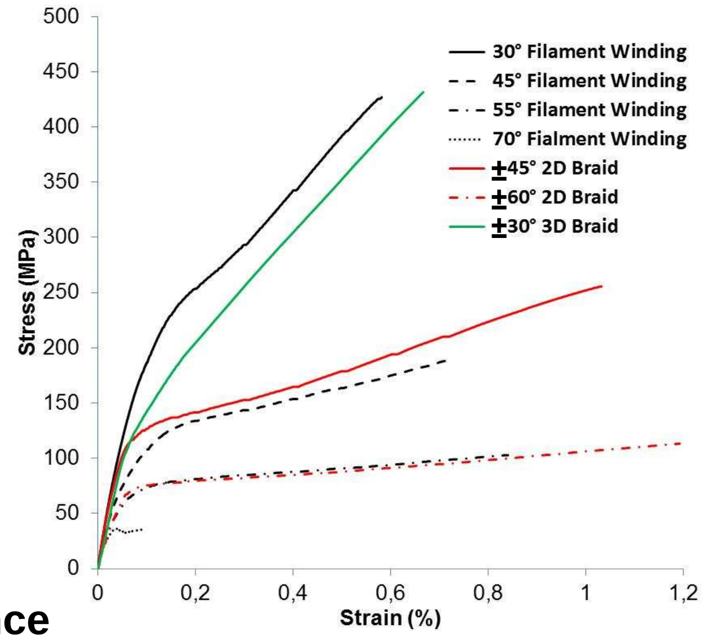
- Consider an elastic/damageable material for the design (with low thermal conductivity)
- Providing gas-tightness (at the level of the cladding, or of the fuel)
- Fabrication of elongated clads
- Describe the oxidation phenomena (passive/active) and consider erosion mechanism
  - o Avoid surface spoiling in nominal condition
  - o Determine the gazeous species induced by LOCA

SiC/SiC cladding mainly driven by GRFs applications

- Significant R&D at CEA in terms of fabrication of suitable cladding (3 patents)
- Tailorable mechanical properties thanks to optimizations of interphase and texture studies
- Very good dimension control and fabrication reproducibility



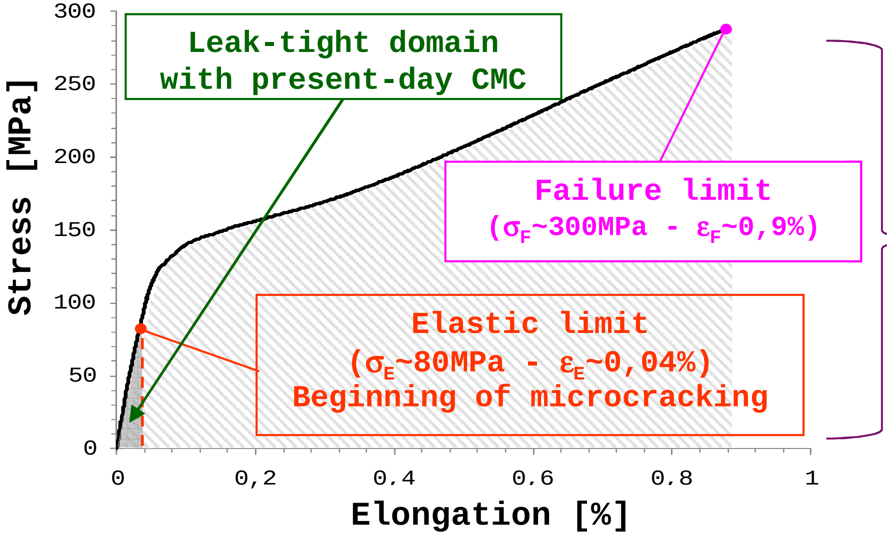




External and internal dimensions with 0,01mm tolerance

SiC/SiC sandwich concept (French patent FR2978697)

All steps of the fabrication process done at CEA

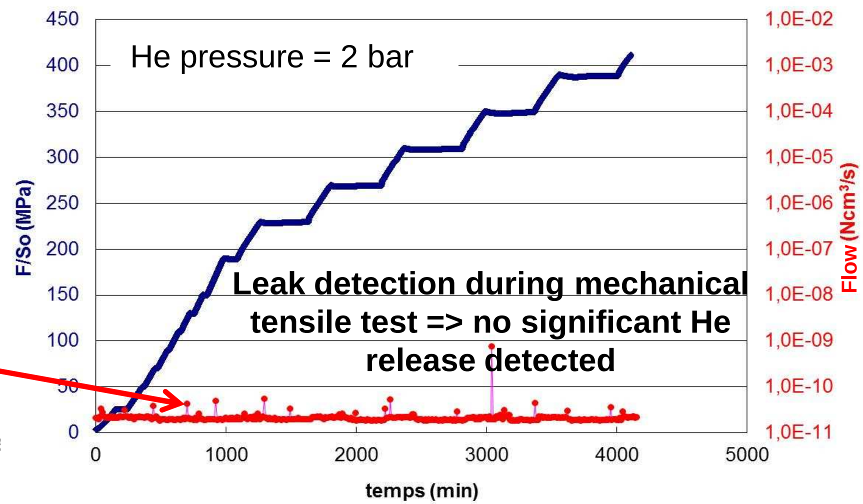


Mechanical behavior remains the same up to at least 1300℃

GFR design:

Internal tube SiC/SiC:	***e~0.3mm***
liner Ta :	***e<0.1mm***
External tube SiC/SiC:	***e~0.6mm***

- **Metallic liner only ensures tightness up to failure limit**
- **Composite ensures mechanical resistance**
- **Process is simple and reproducible**
- **End-plugging solutions (welding)**

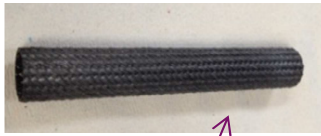


Leak detection limit

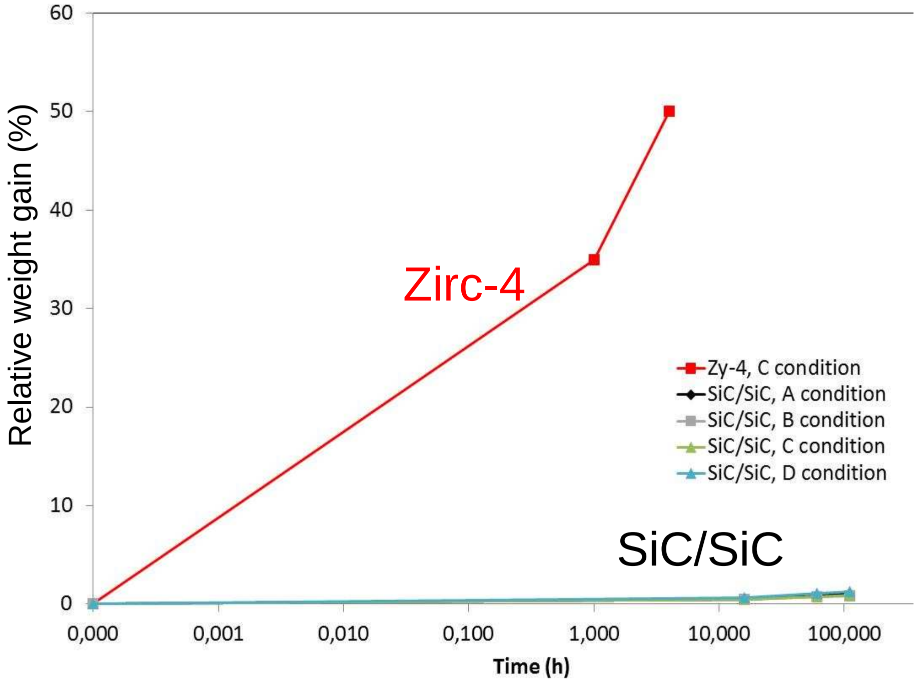
Preliminary High Temperature testing of SiC/SiC for PWR

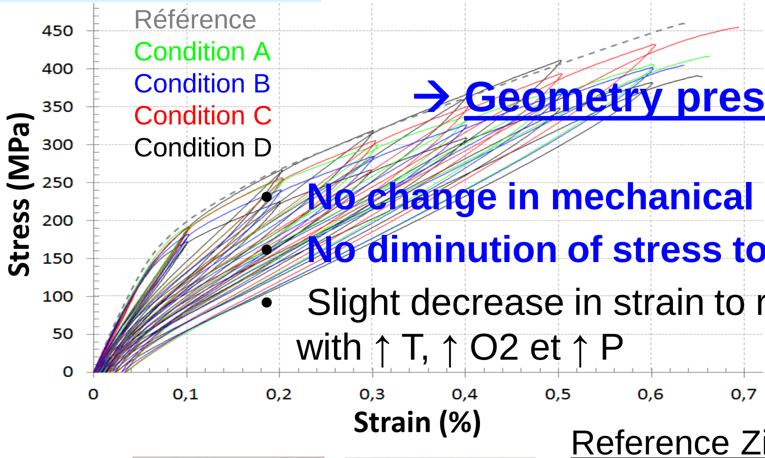
SiC/SiC tubes and SiC wafers (A to C)	Condition A	1 MPa – 1200°C – Air/H_2O (95/5)
	Condition B	0,1 MPa – 1200°C – O_2/H_2O (50/50)
	Condition C	0,1 MPa – 1200°C – Air/H_2O (50/50)
	Condition D	0,1 MPa – 1400°C – Air/H_2O (50/50)
Zircaloy clad →	Condition C	0,1 MPa – 1200°C – Air/H_2O (50/50)

% O_2 ↗

Before / After testing





→ Geometry preservation

- **No change in mechanical behavior**
- **No diminution of stress to rupture**
- Slight decrease in strain to rupture with ↑ T, ↑ O2 et ↑ P

Reference Zirc-4 cladding after a few hours at 1200°C:
- Loss of geometry
- Full wall thickness Cracking…

= well-known results (CEA, ANL, KIT, JAEA, etc…)

Preliminar nominal Temperature corrosion testing of SiC/SiC for PWR

- SiC/SiC tubes nominal conditions (T= 360℃ and P = 180 bars) during **3500h = 5 months**
- Comparison with high purity monolithic CVD β-SiC samples (⇔ CVI matrix of SiC/SiC)
- Effect of water chemical composition (2 autoclaves)

1. Distilled water (DW) **2. LWR water composition** (1000 ppm H_3BO_3 and 2 ppm LiOH)

CVD β-SiC and SiC/SiC materials description

- **Monolithic CVD β-SiC**
- **Hi-Nicalon S fibers reinforced SiC/SiC tubular composites (CEA production)**

- Undamaged and pre-damaged (at different levels) SiC/SiC in both autoclaves

→ Access to Pyrocarbon interphase oxidation allowed

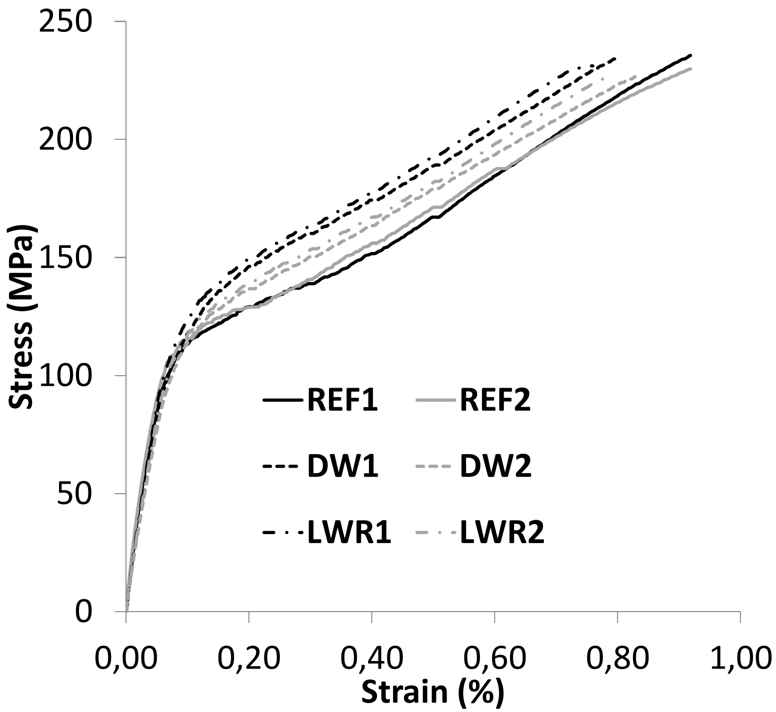
Weight changes

Sample name	DW_{REF}	$DW_{0.05\%}$	$DW_{0.1\%}$	$DW_{0.15\%}$	$DW_{0.3\%}$	DW_{CVD}	LWR_{REF}	$LWR_{0.05\%}$	$LWR_{0.1\%}$	$LWR_{0.15\%}$	$LWR_{0.3\%}$	LWR_{CVD}
Weight change (%)	**-0.04**	0.06	-0.73	-0.99	-0.58	**-0,18**	**-0.03**	0.02	-0.91	-0.78	-0.45	**-0.12**
			Possible loss of particles during experiment and/or washing!									

- No significant effect of water composition

- Very low weight loss for undamaged materials ⇒ No passive oxidation (weight gain)

Mechanical behavior of undamaged composites



Sample	Failure stress σ_R (MPa)	Failure strain (%)
REFs	235	0,92
$DW_{undamaged}$	231	0,82
$LWR_{undamaged}$	228	0,78
$DW_{pre\text{-}damaged}$	221	0,82
$LWR_{pre\text{-}damaged}$	220	0,81

- No reduction of tensile strength for undamaged materials
- Very low reduction of tensile strength for pre-damaged (up to 0,3%) materials (~5%) ⇔ No significant effect of pre-damaging compare to reference specimens

Pyrocarbon interphase is not significantly degraded for these oxidation conditions

Chemical composition of water before and after oxidation treatments

Elements	Dw_{before} (ppb)	Dw_{after} (ppb)	LWR_{before} (ppb)	LWR_{after} (ppb)
B	8,4	13,4	1007 ppm	966 ppm
Li	<0,001	0,86	1954	509
Si	<LQ	84ppm	<LQ	68 ppm
pH	7,02	8,3	7,48	7,89

- Si comes from SiC/SiC and concentrations correspond to solubility limit of SiO_2 in water at 25℃ (0,12-0,14g/l).

Status of the R&D on innovative SiC/SiC cladding for PWR at CEA

- Sandwich SiC/SiC cladding must be suitable for PWR
- SiC/SiC resistance to high temperature oxidation (air/O_2) is demonstrated
- Preliminary SiC/SiC corrosion tests in nominal conditions are promising

Good results obtained so far BUT → **Long-term studies needed to confirm the efficiency of SiC/SiC for PWR cladding application**

Further work, pending issues

- Optimization of the sandwich tube to LWR requirements (definition of the best liner)
- Assessment of corrosion resistance both in nominal and accidental conditions - more analytical/fundamental studies needed: Thermodynamics, kinetics…
  - o Gazeous species detection (H_2 risk) (*)
  - o Integral tests with fuel up to melting (*)
- Characterization/optimization of the mechanical properties in nominal and accidental conditions
- Fretting/erosion studies
- Evaluation of the neutronic impact
- Thermomechanical simulations
- Fabrication of >1m cladding

} Optimal parameters to define a reference core

- **Neutron irradiation behavior in representative PWR environment + power ramp tests including relevant PIE and semi-integral LOCA tests**…(*)
- **Other incidental/accidental scenarii** (RIA, etc…) (*)

(*) *Topics where international collaboration could be of interest…*

Thank you for your attention

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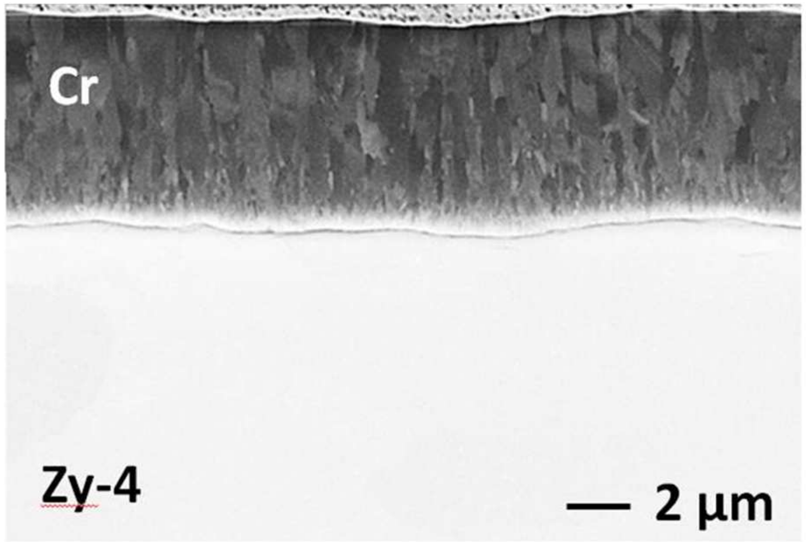
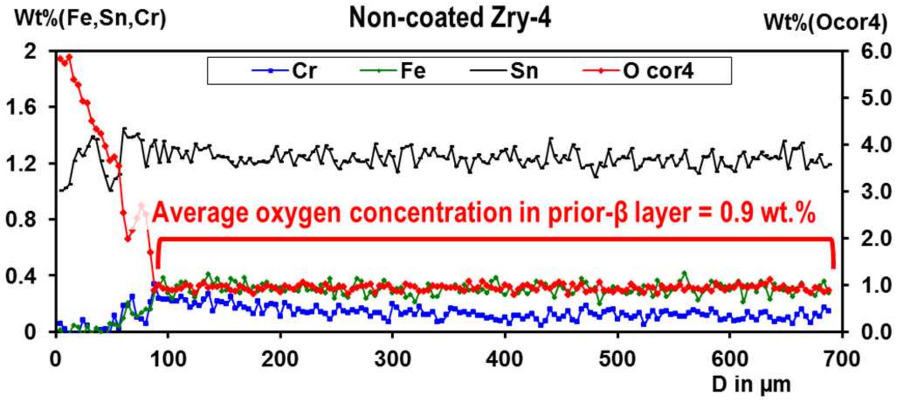
Back-up slides

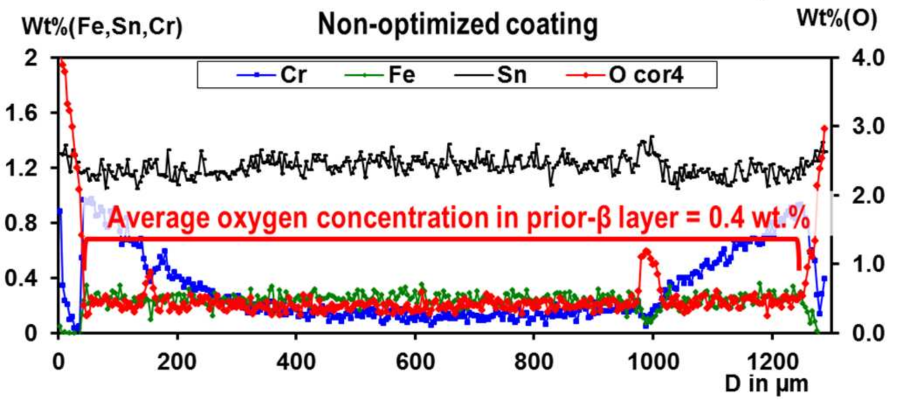
Samples preparation

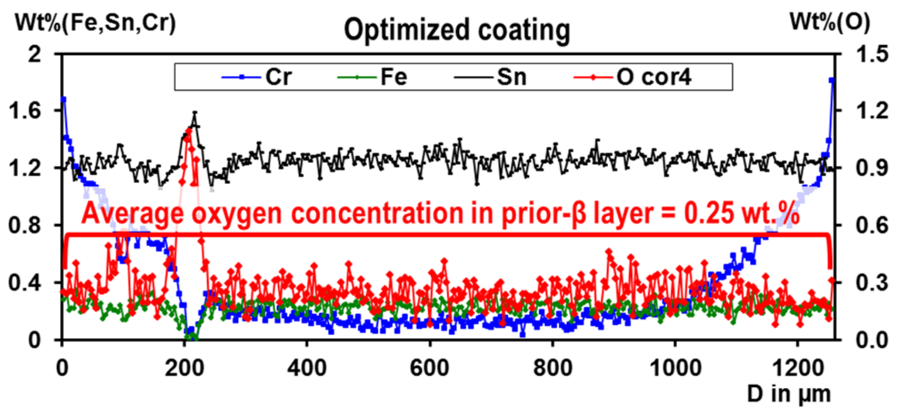
- Flat specimens of SRA low tin Zy-4 (45x14x13 mm)
- Coated on both sides by PVD (Physical Vapor Deposition)



CHEMICAL ELEMENTS DIFFUSION PROFILES (EPMA MEASUREMENTS)

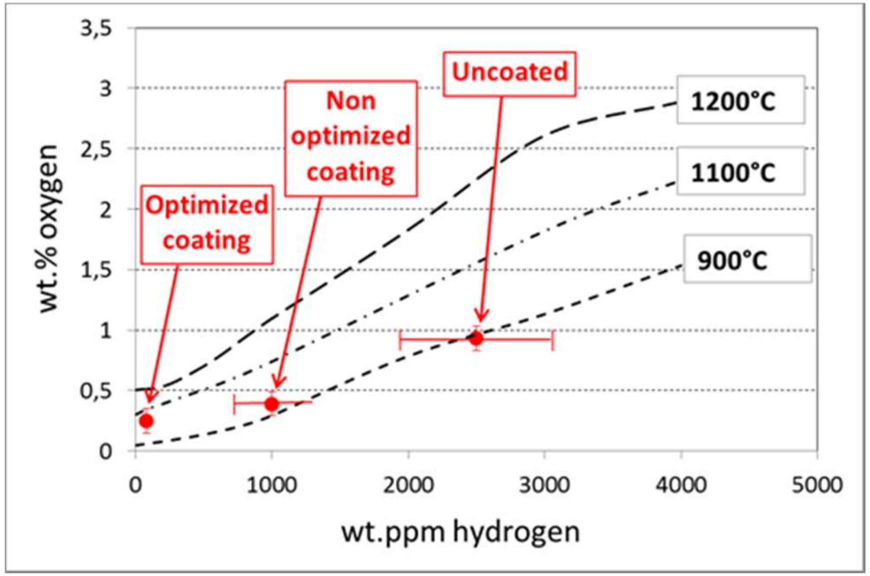






Significant increase of oxygen content in the beta phase for un-coated Zy-4

	Un-coated Zry-4	Non optimized coating	Optimized coating
HV(50g)	~450 (+/-50)	~320 (+/-35)	~215 (+/-15)



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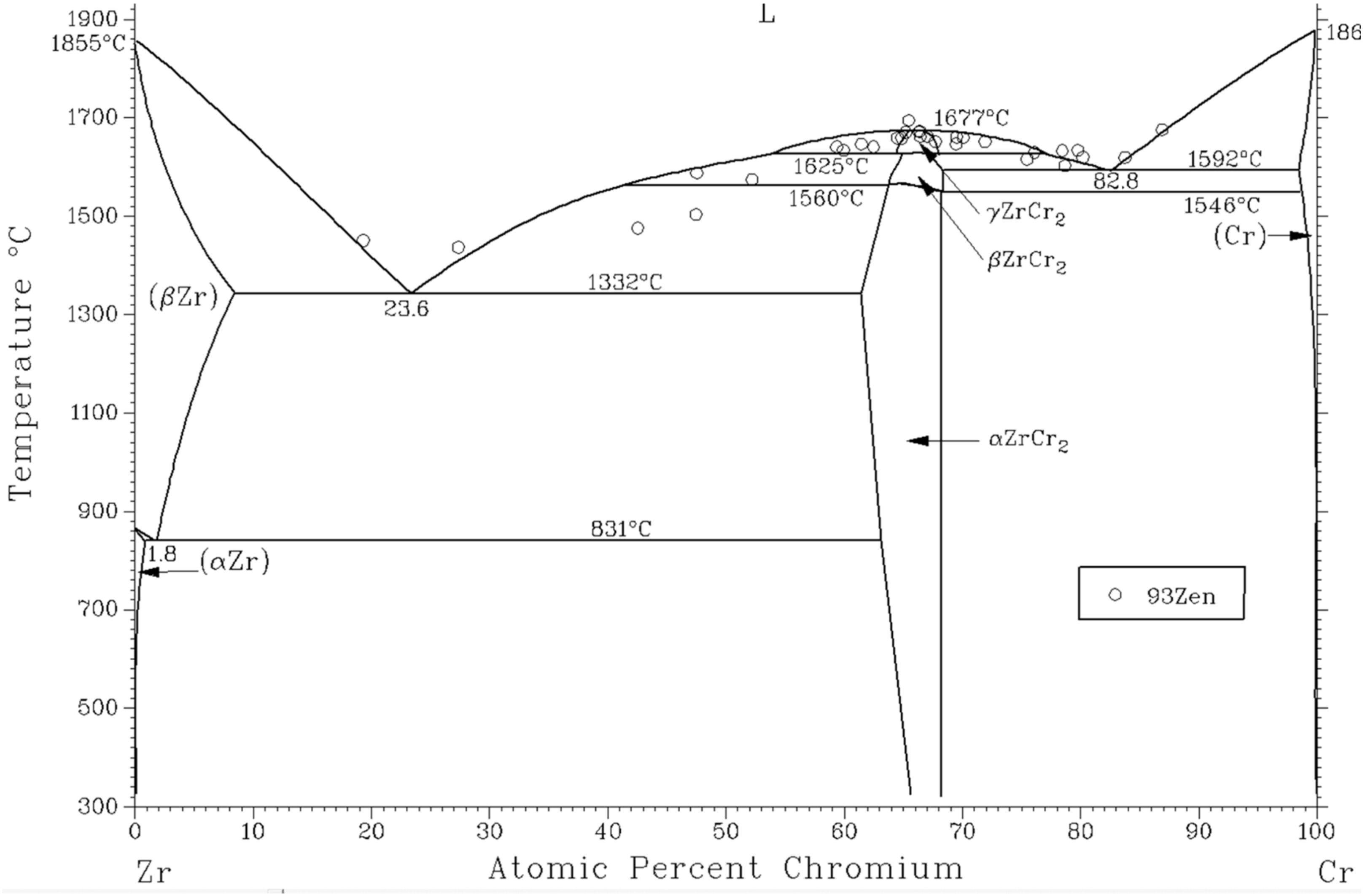
L
1900
1855°C
1700
1500
1300
1100
900
700
500
300
186
1677°C
1625°C
1560°C
1592°C
82.8
1546°C
γZrCr2
βZrCr2
(Cr)
(βZr)
23.6
1332°C
αZrCr2
831°C
1.8
(αZr)
93Zen
Temperature °C
0
10
20
30
40
50
60
70
80
90
100
Zr
Atomic Percent Chromium
Cr