HIGH TEMPERATURE OXIDATION OF E110 ALLOY WITH FeCrNi AND CrNi BASED COATINGS

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Introduction

First stage of all ATF-programs including ROSATOM – is **modification and coatings deposition** on Zr (E110) claddings.

ROSATOM

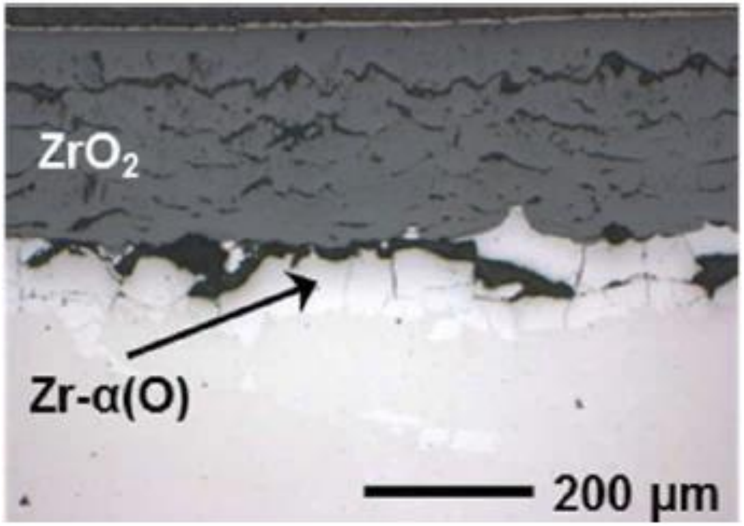
AREVA forward-looking energy

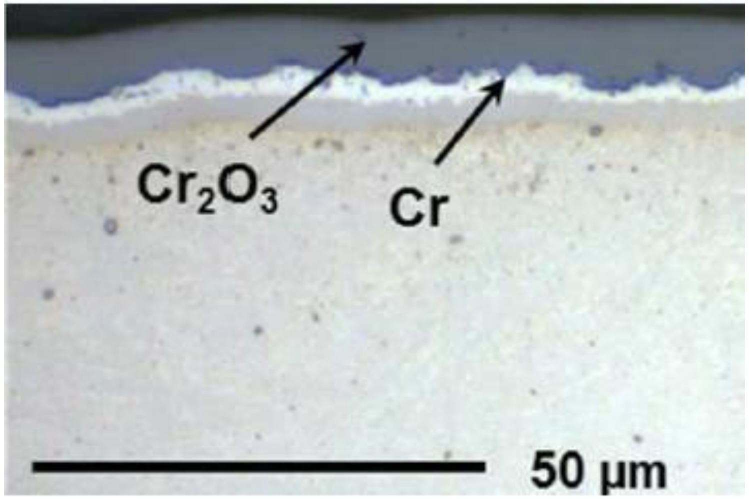
Westinghouse

KAERI Korea Atomic Energy Research Institute

Introduction

Cr-based coatings are investigated actively because of dense Cr_2O_3 layer forming during high-temperature oxidation.





Zry-4 uncoated (left) and Cr-coated (right) after steam oxidation 1200 ºC 15000 s (P. Guillermier – IAEA 2015)

The main goal

To investigate the effectiveness of **anticorrosion Cr-content coatings** on fuel claddings from E110 alloy

1. Batch of samples were prepared:
   Ø 9.1 / 9.5 mm, 10-500 mm length
   total amount about 300

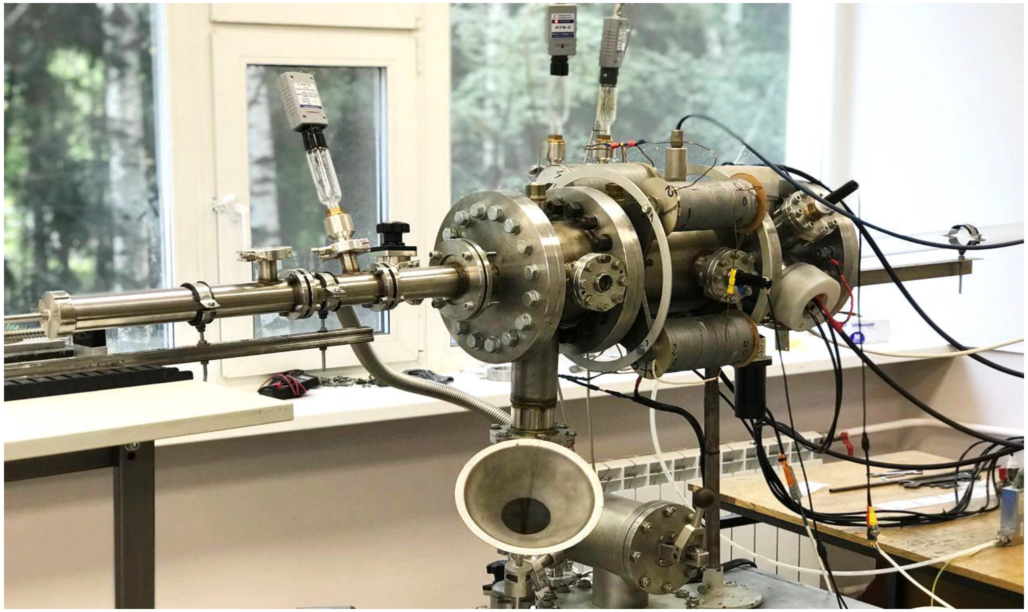
2. Corrosion tests were performed:
   autoclave
   LOCA conditions

3. Material state was analyzed

4. **Fuel assemblies with coated samples were made for tests in MIR research reactor (now in progress)**

Coatings deposition

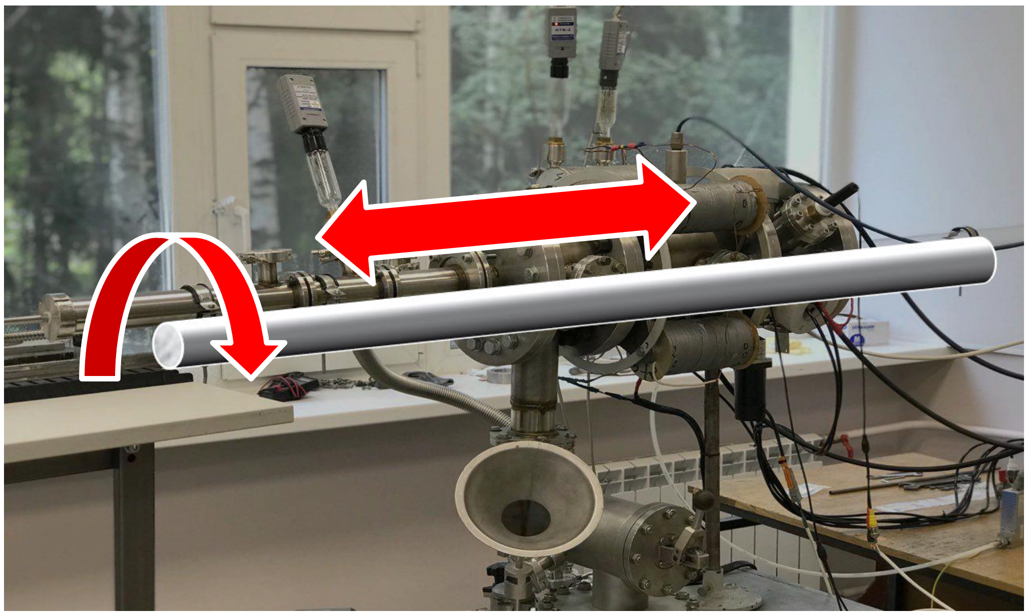
Coatings were deposited on claddings outer surface by ion-plasma methods.



Installations for claddings ion-plasma treatment ILUR-03 (up) and KVK-10 (right)

Coatings deposition

Coatings homogeneity provided by technology: translational motion and axial rotation of samples.

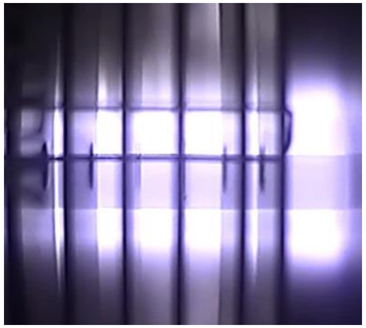


Installations for claddings ion-plasma treatment ILUR-03 (up) and KVK-10 (right)

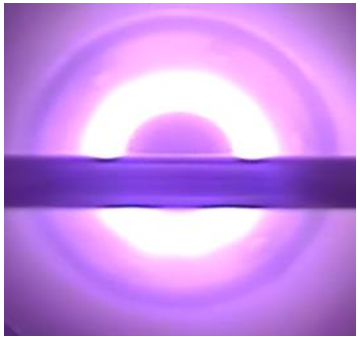
Coatings deposition

Coatings were deposited by several stages:

1. Pre-treatment by Ar^+ E = 0.1-1.0 keV



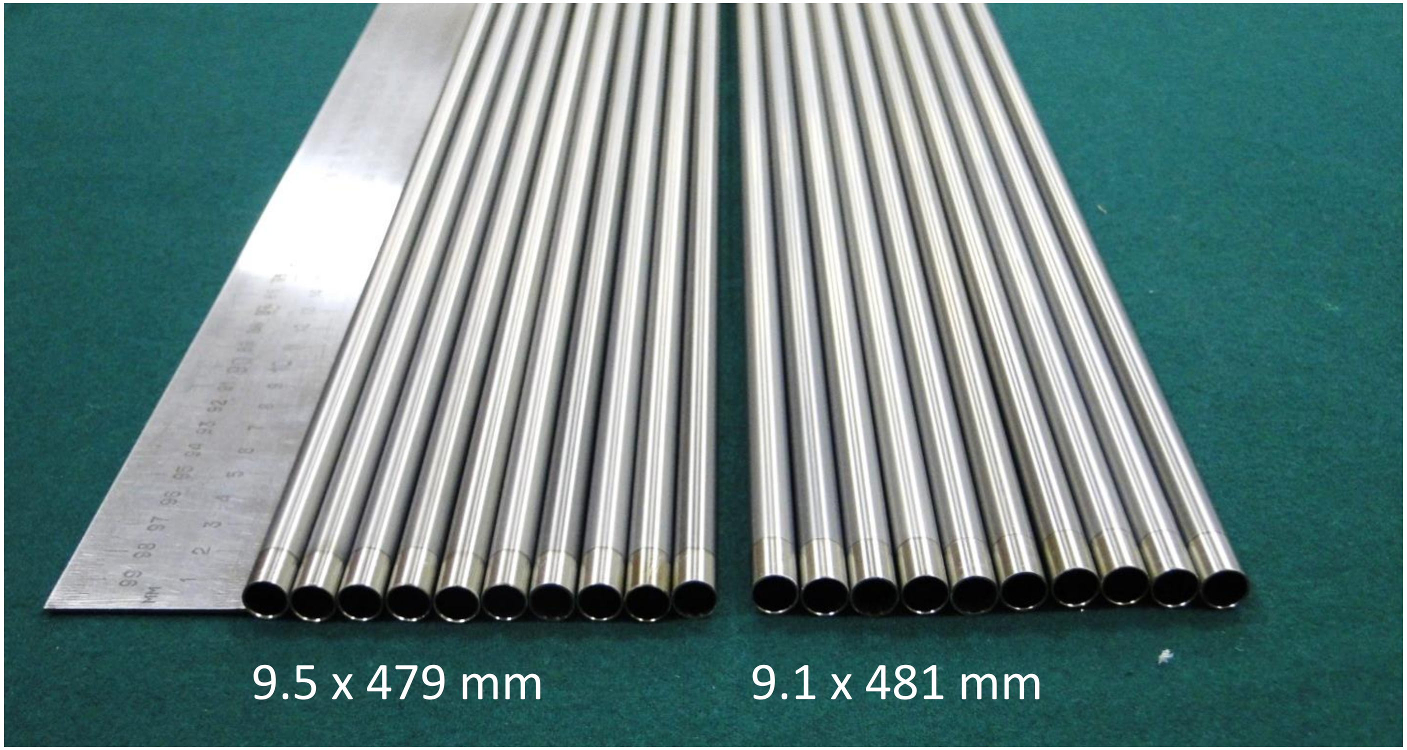
2. Multilayer magnetron deposition



* Additional bombardment by Ar^+ E = 35 keV
(on KVK-10 only)

Coatings deposition

Coating base	Max thickness, µm
Cr	10±1
FeCrNi	7±1
NiCr	10±1



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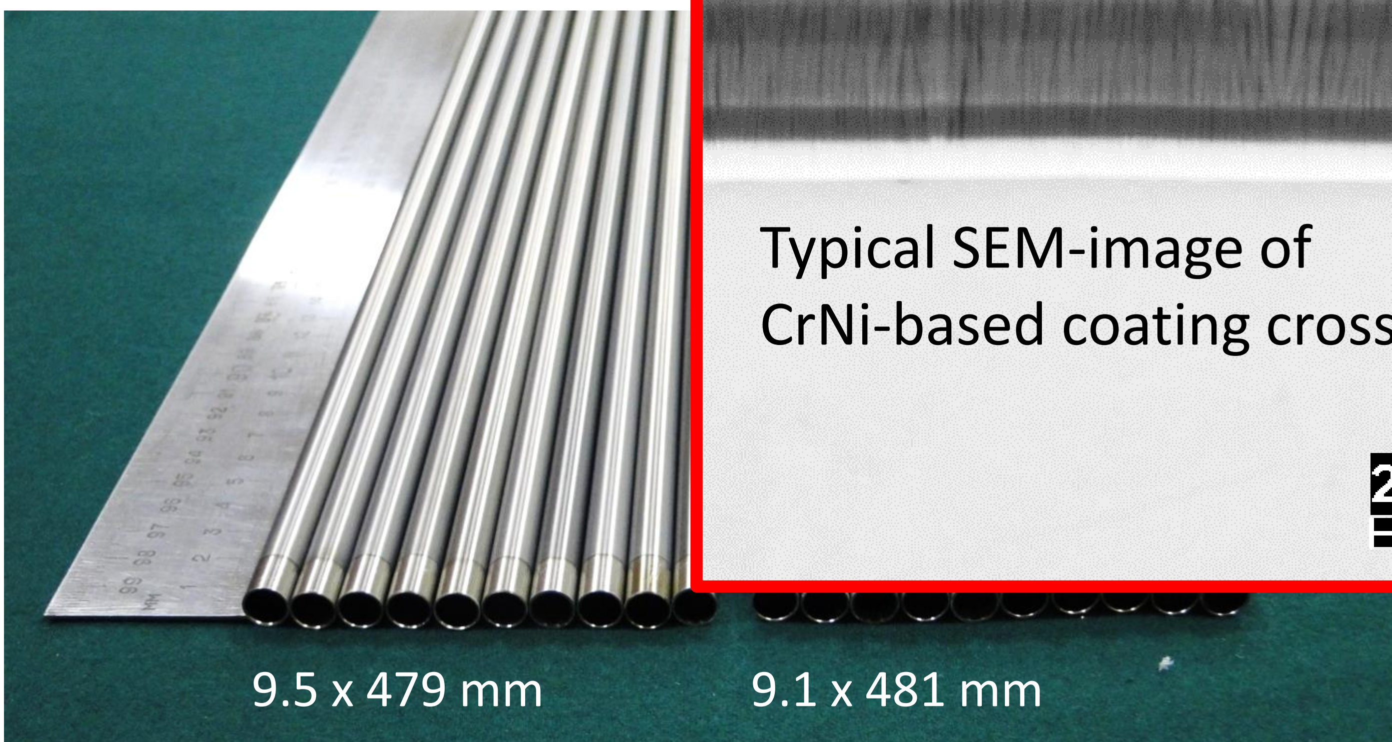
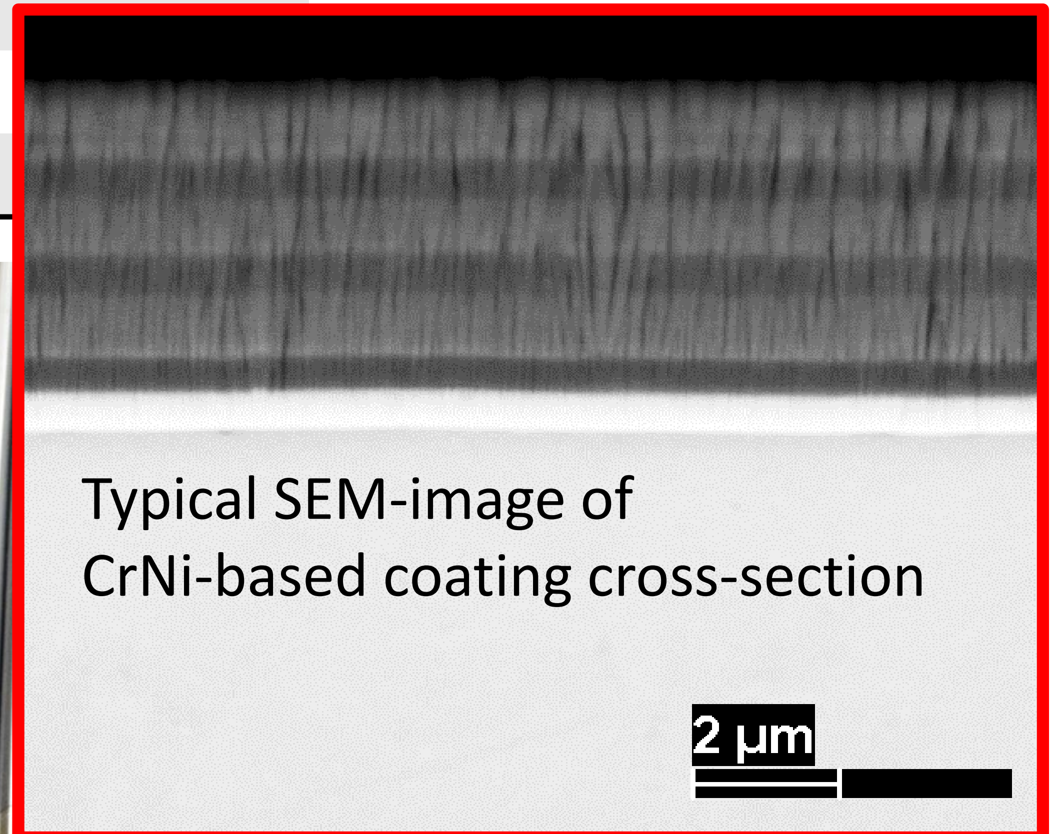
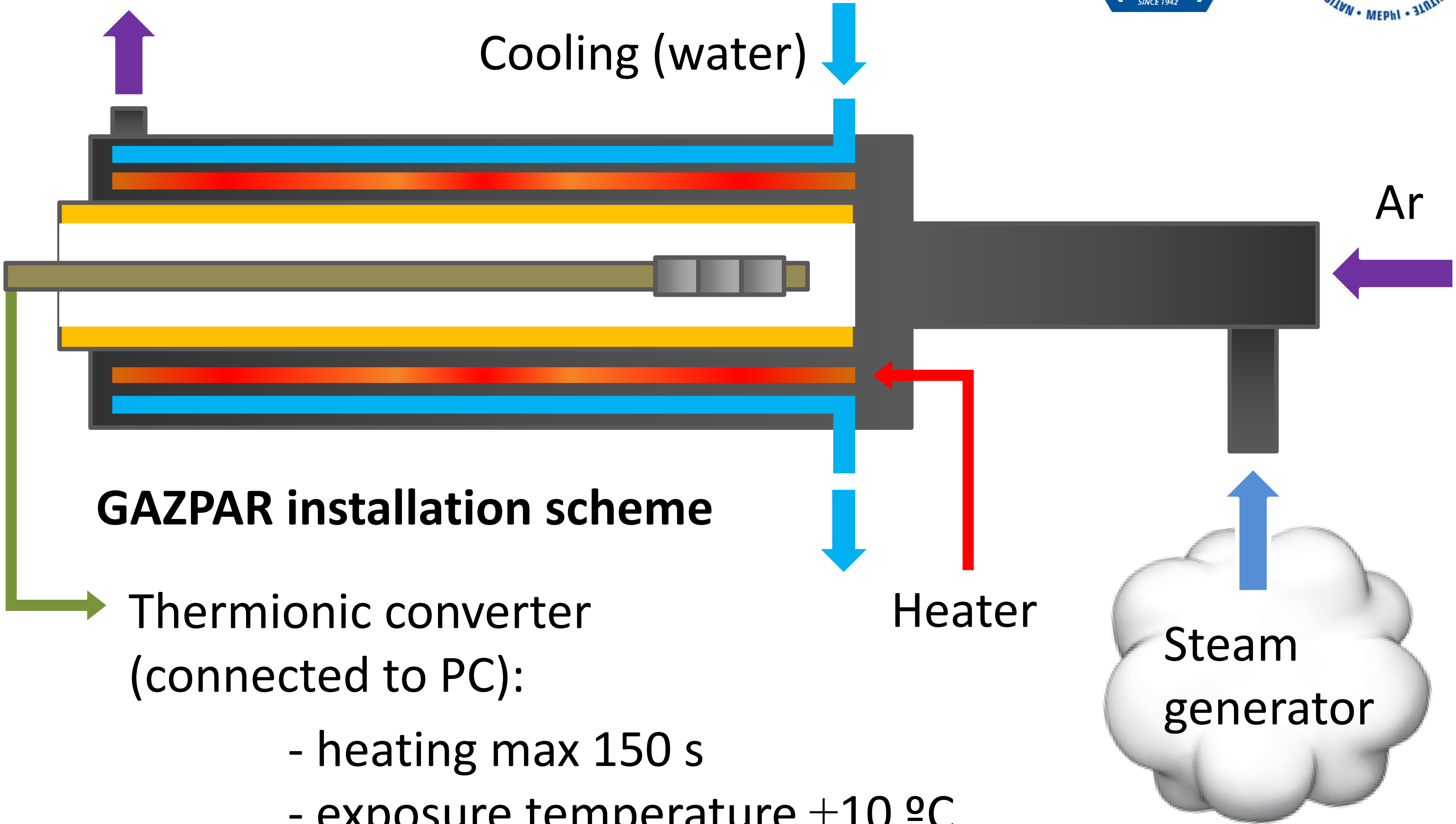




Typical SEM-image of CrNi-based coating cross-section

High-temperature corrosion

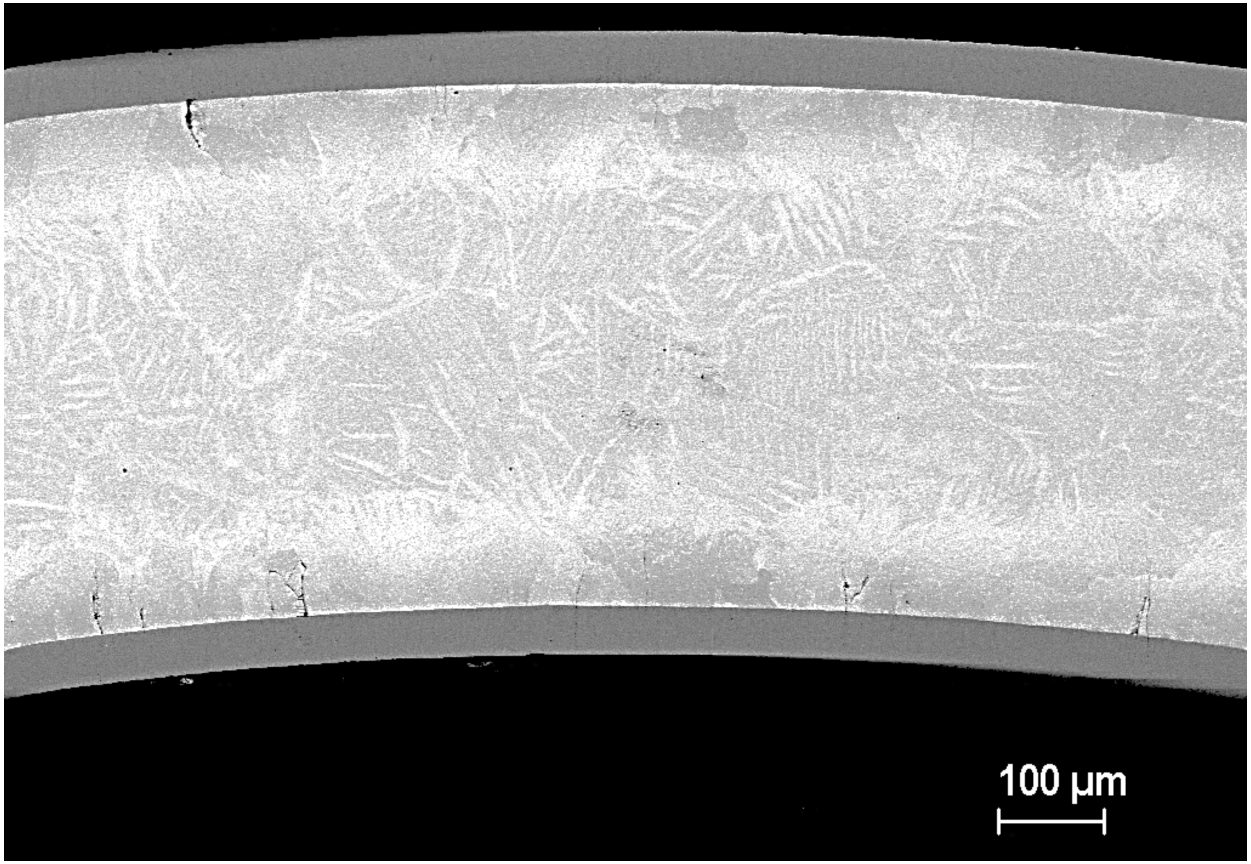


GAZPAR installation scheme

Thermionic converter (connected to PC):

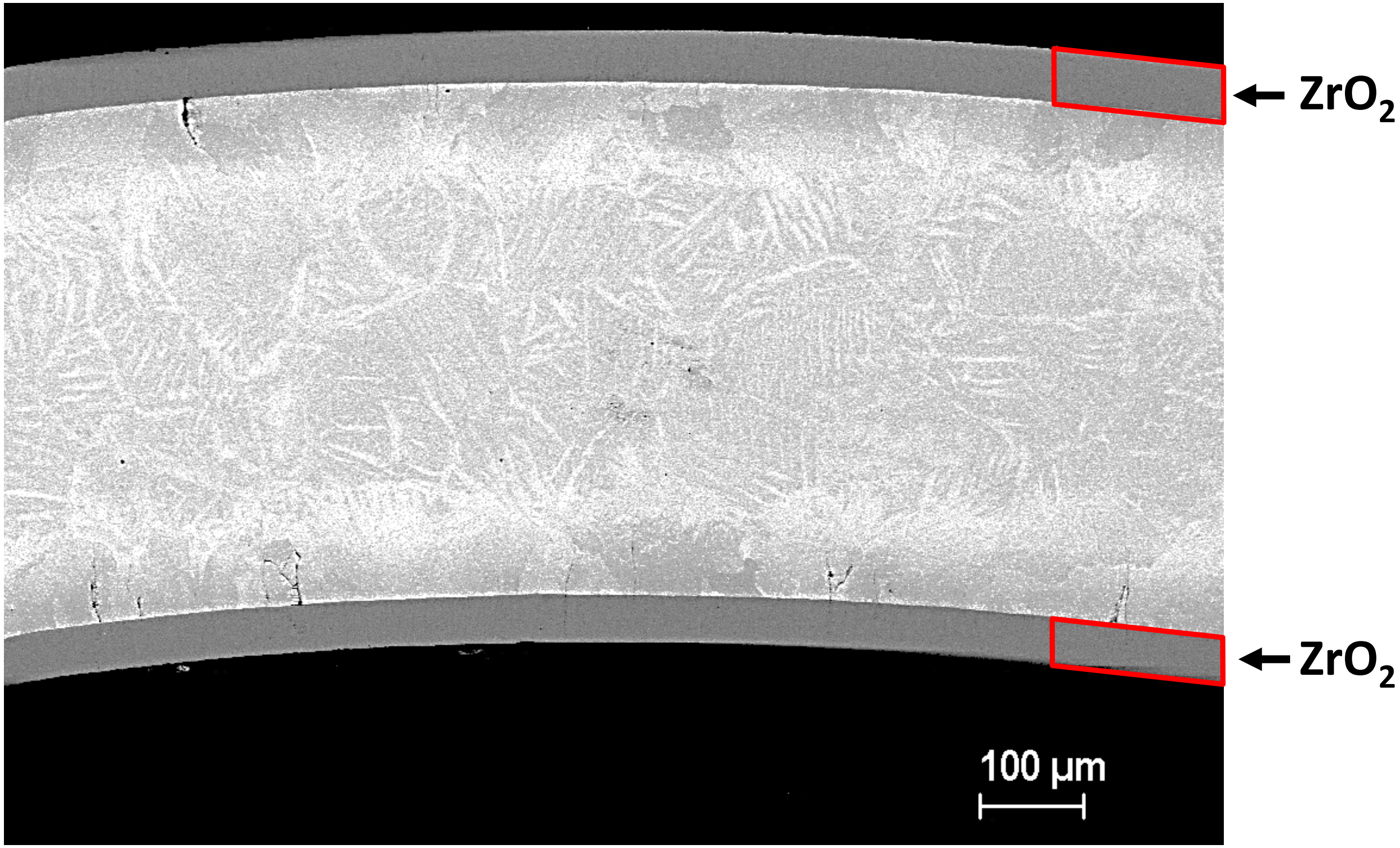
- heating max 150 s
- exposure temperature ±10 ºC
- cooling min 20 ºC/s

Uncoated E110 corrosion



Typical SEM-image of E110 cladding cross-section after oxidation 1200 ºC 500 s

Uncoated E110 corrosion



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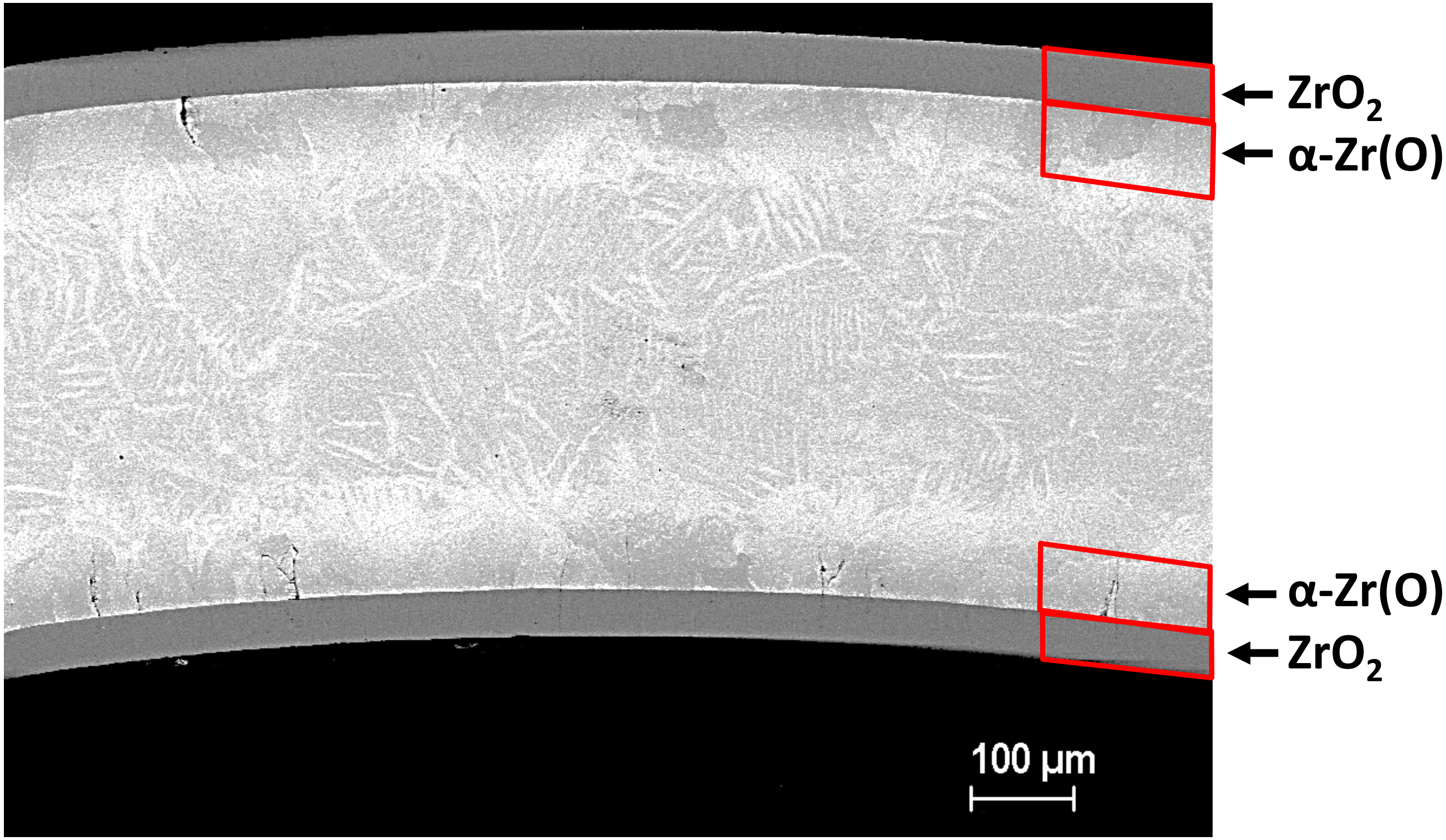

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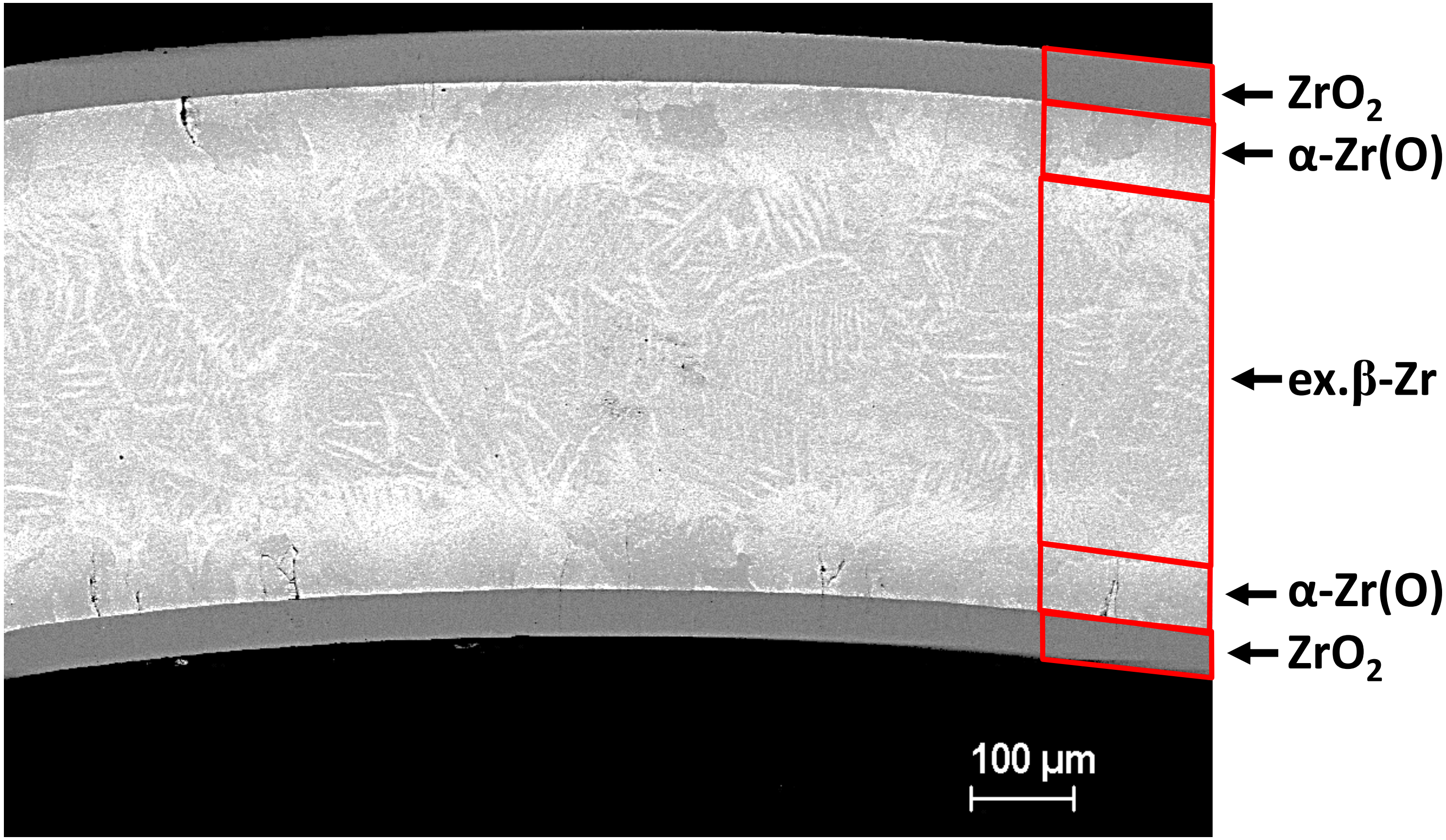
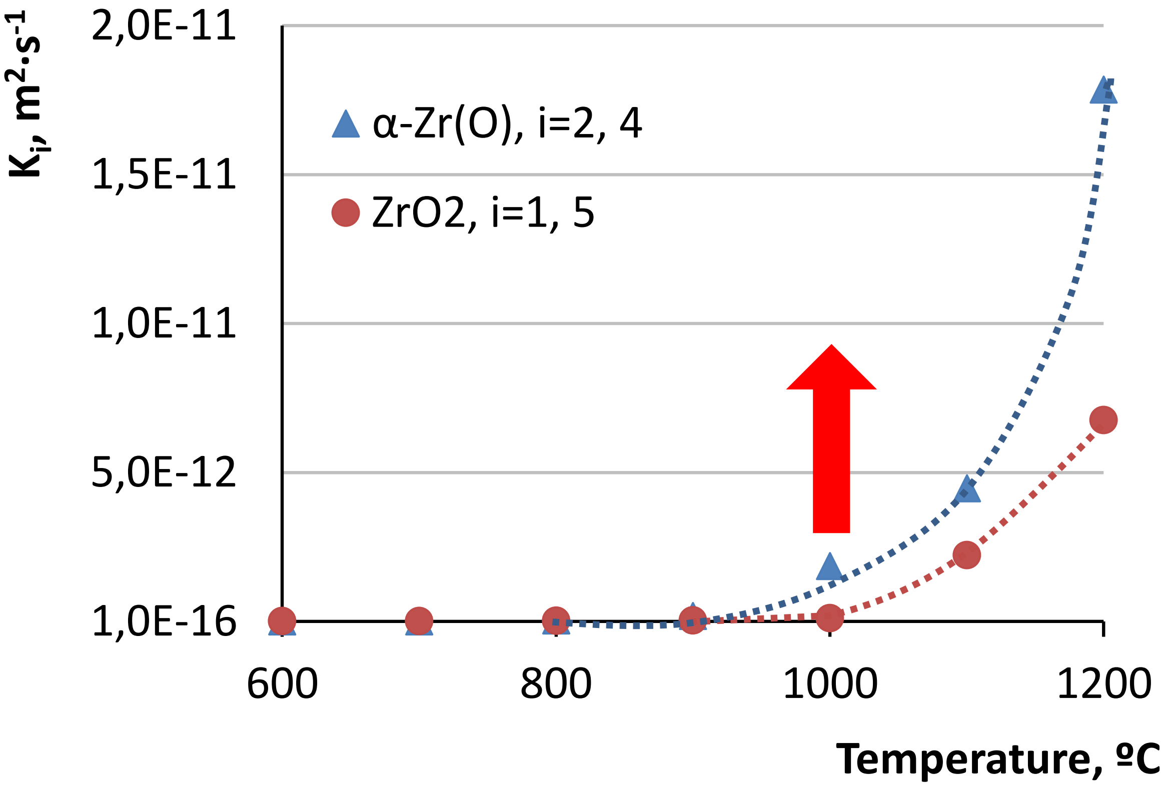


Typical SEM-image of E110 cladding cross-section after oxidation 1200 ºC 500 s

Uncoated E110 corrosion



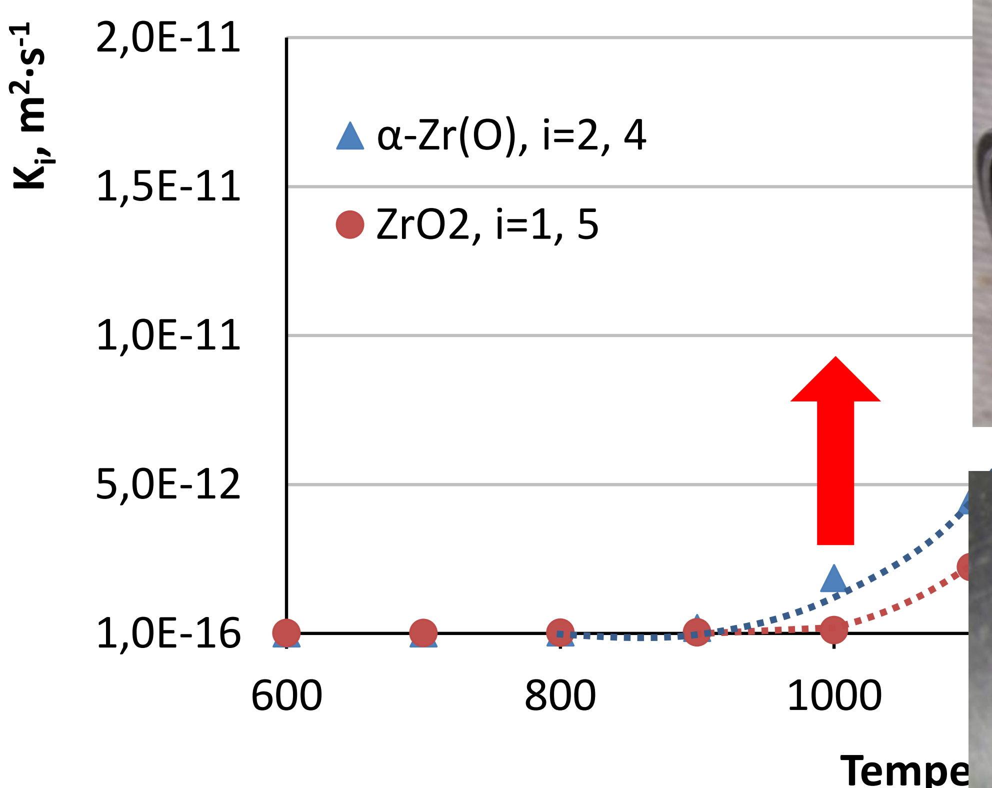
Phenomenological description:

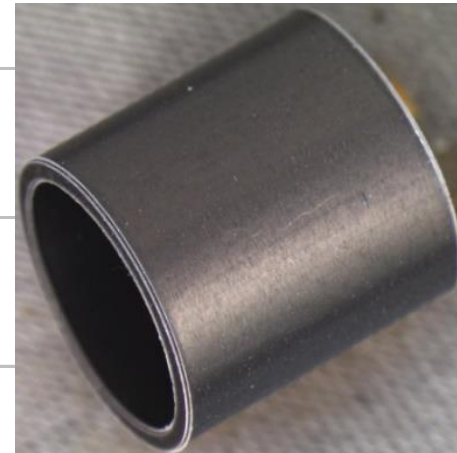
$$x_i^2 = K_i \cdot t$$

x_i – *i*-zone thickness
K_i – growth constant
t – exposure time

Oxygen penetration rate increases about 10^4-10^5 times with increasing exposure temperature above 1000 ºC

Uncoated E110 corrosion





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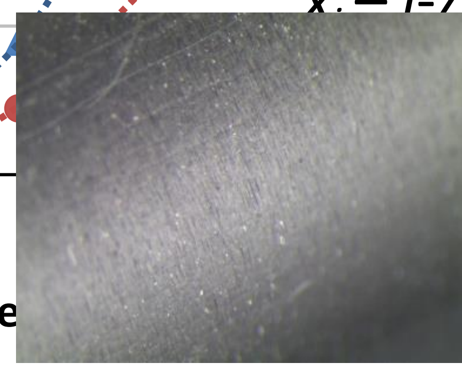
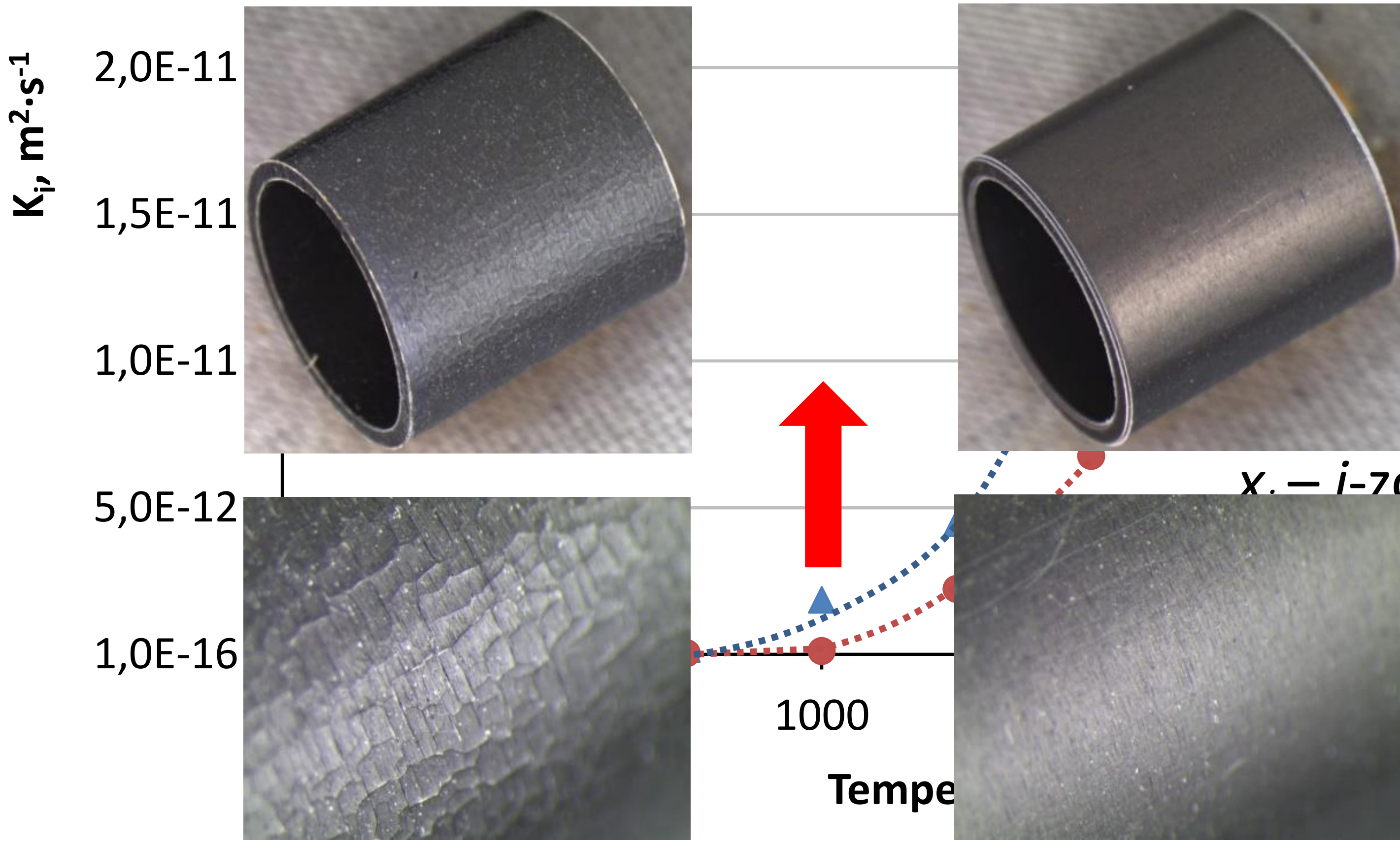


Uniform oxide
1200 ºC ECR = 27.9 %

Uncoated E110 corrosion



menological

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$\cdot t$

x_i – *i*-zone thickness

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Cracks in oxide
800 ºC ECR = 5.1 %

Uniform oxide
1200 ºC ECR = 27.9 %

Cr-coatings at 800 ºC

Oxidation conditions	Uncoated E110	Cr 2-4 µm	Cr 8-10 µm
800 ºC 5000 s	ECR = 2.1 %	ECR = 1.5 %	ECR = 1.4 %
800 ºC 7500 s	ECR = 3.3 %	ECR = 1.6 %	ECR = 2.3 %
1000 ºC 5000 s	ECR = 5.3 %	ECR = 5.9 %	-

To study how **internal stresses caused by α-β transformation** effect on the chromium coatings preliminary experiments were carried out.

Cr-coatings at 800 ºC

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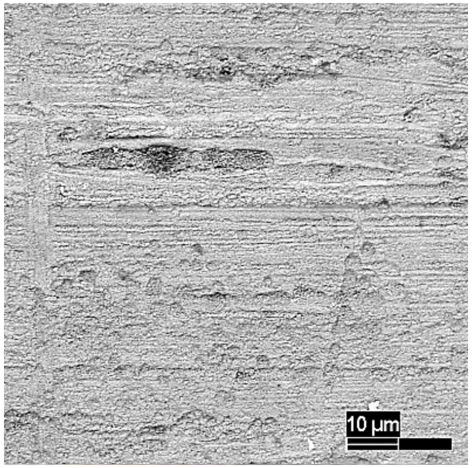
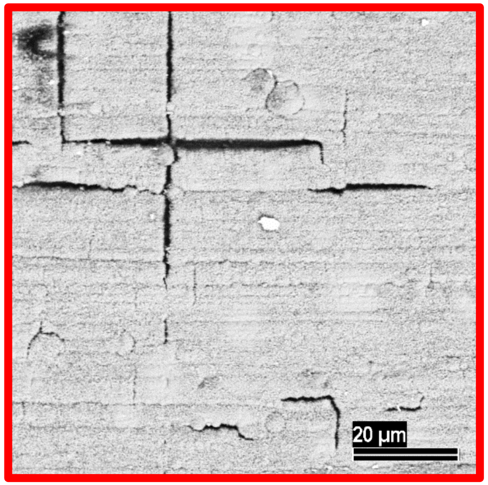
1000 ºC 5000 s	ECR = 5.3 %	ECR = 5.9 %	-

ECR increases due to **microcracks** formation





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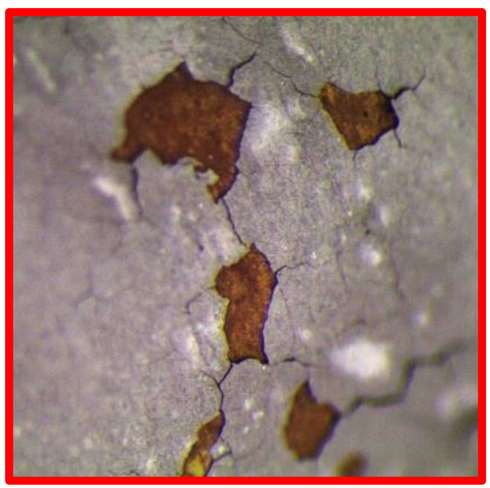
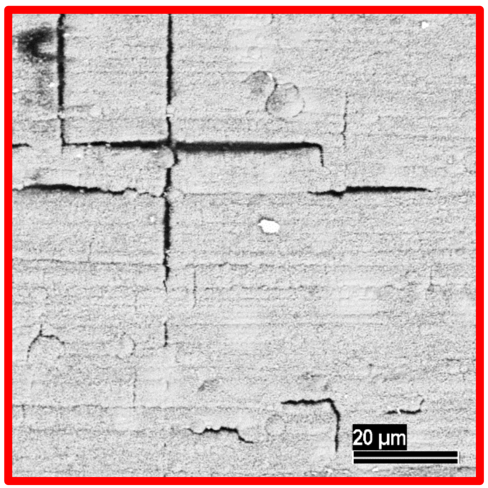
1000 ºC 5000 s	ECR = 5.3 %	ECR = 5.9 %	-

Cr-coating 2-4 µm is not enough to protect Zr





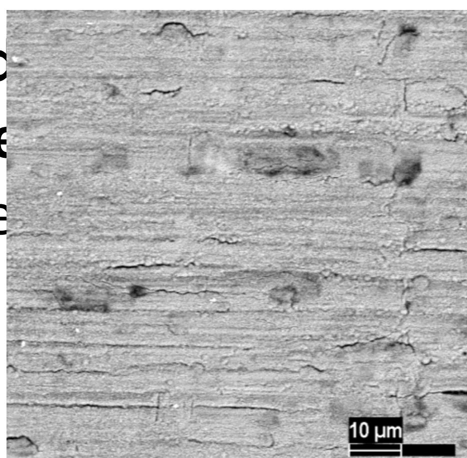
FeCrNi-coatings at 800 ºC

Oxidation conditions	Uncoated E110	FeCrNi 2-4 µm
800 ºC 5000 s	ECR = 2.1 %	ECR = 1.7 %
800 ºC 7500 s	ECR = 3.3 %	ECR = 2.5 %
1000 ºC 5000 s	ECR = 5.3 %	ECR = 5.1 %

No destructions at the same conditions, but **lower efficiency** compare with Cr-coatings, especially at higher temperature.

FeCrNi-coatings at 800 ºC

Oxidation conditions	Uncoated E110	FeCrNi 2-4 µm
800 ºC 5000 s	ECR = 2.1 %	ECR = 1.7 %
800 ºC 7500 s	ECR = 3.3 %	ECR = 2.5 %
1000 ºC 5000 s	ECR = 5.3 %	ECR = 5.1 %

No c   **bu**

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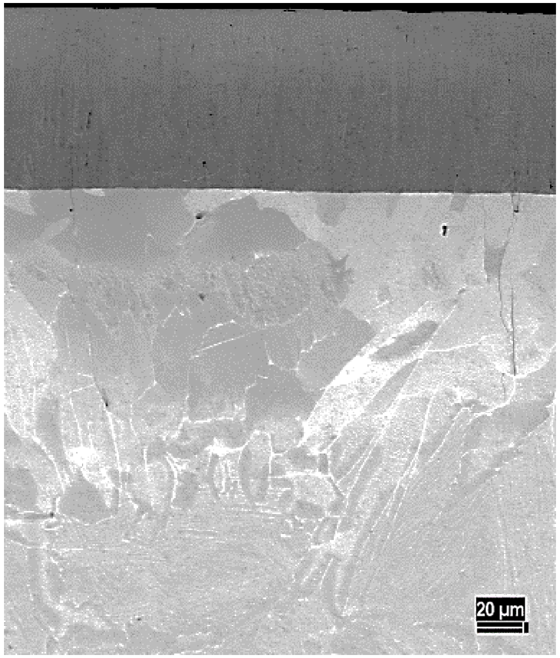
Cr/FeCrNi/Cr and Cr/CrNi/Cr

Composition	Thickness, µm	ECR, %
uncoated	-	17.3
Cr/FeCrNi/Cr	1.0±0.3	17.4
Cr/FeCrNi/Cr	2.9±0.3	18.4
Cr/FeCrNi/Cr	3.9±0.3	19.0
Cr/FeCrNi/Cr	4.3±0.3	19.0
Cr/FeCrNi/CrNi	7.0±0.3	13.5
Cr/CrNi/Cr	1.0±0.3	17.4
Cr/CrNi/Cr	4.5±0.3	12.4
Cr/CrNi/Cr	6.5±0.3	11.5
Cr/CrNi/Cr	8.7±0.3	10.1
Cr/CrNi/Cr	9.8±0.3	9.6
Cr/CrNi/Cr	10.8±0.3	10.7

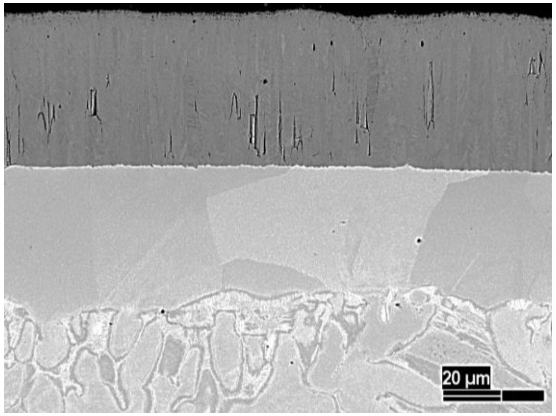
ECR calculated by weight gain shows obscure results

Oxidation at 1200 ºC 400 s

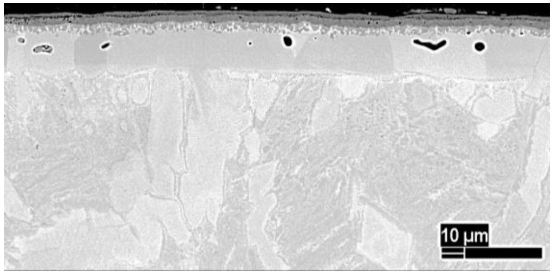
Cr/FeCrNi/Cr and Cr/CrNi/Cr



Uncoated E110
1200 ºC 400 s

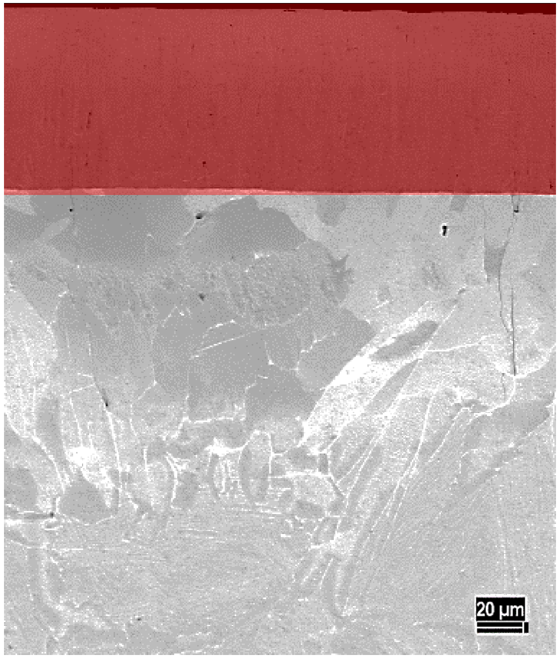


Cr/FeCrNi 4.1±0.3 µm
1200 ºC 400 s

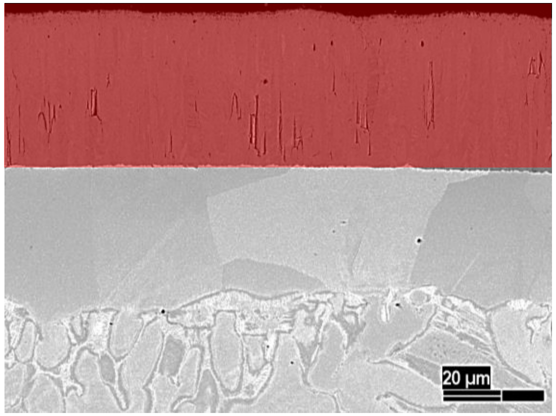


Cr/CrNi 9.8±0.3 µm
1200 ºC 400 s

Cr/FeCrNi/Cr and Cr/CrNi/Cr

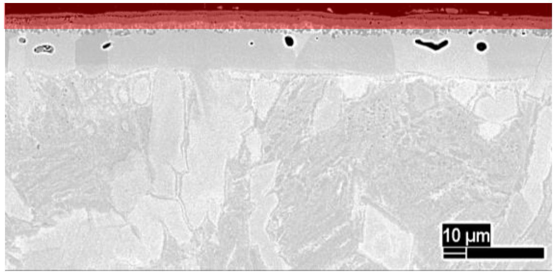


Uncoated E110
1200 ºC 400 s
- ZrO_2 **50±5 µm**



Cr/FeCrNi 4.1±0.3 µm
1200 ºC 400 s

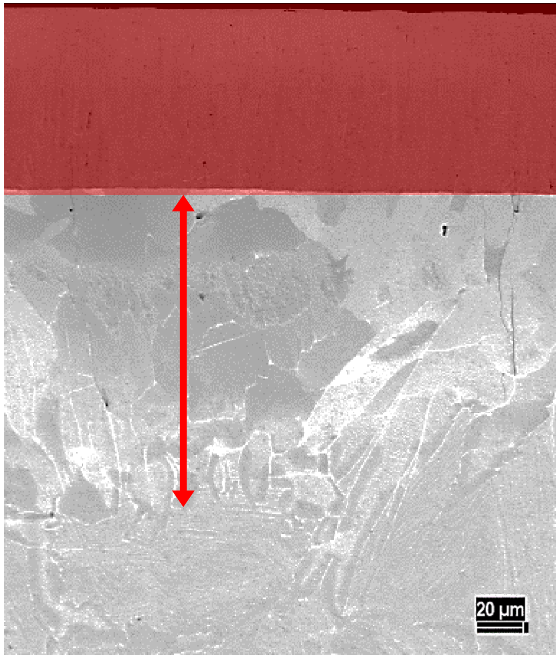
- slightly affect on oxide thickness **10%**



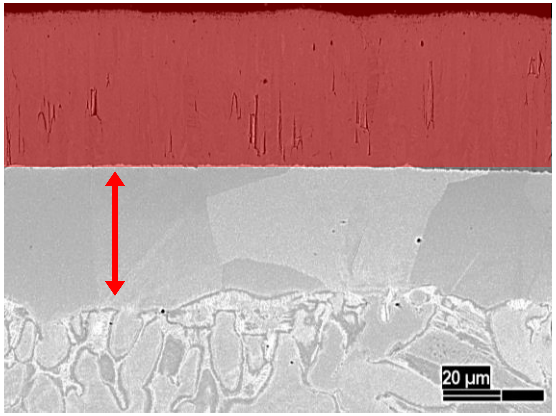
Cr/CrNi 9.8±0.3 µm
1200 ºC 400 s

- decrease oxide zone significantly **70%**

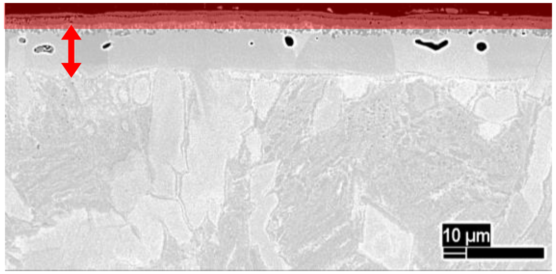
Cr/FeCrNi/Cr and Cr/CrNi/Cr



Uncoated E110
1200 ºC 400 s
- ZrO_2 50±5 µm
- α-Zr(O) **80±10 µm**

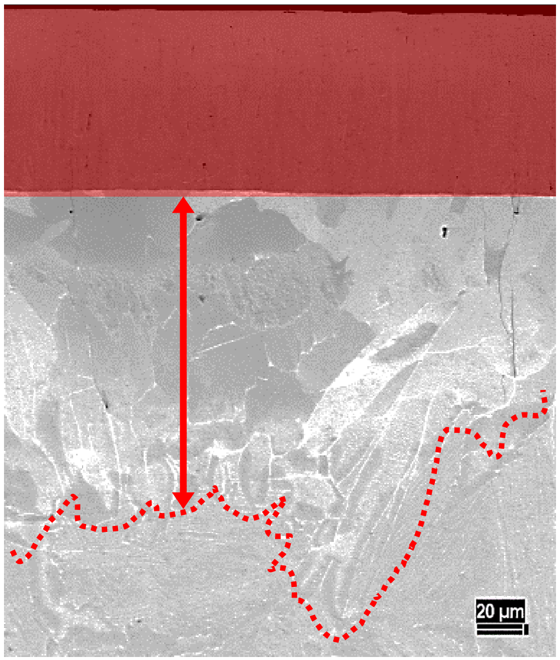


Cr/FeCrNi 4.1±0.3 µm
1200 ºC 400 s
- slightly affect on oxide thickness **10%**
- decrease α-Zr(O) layer size **30%**

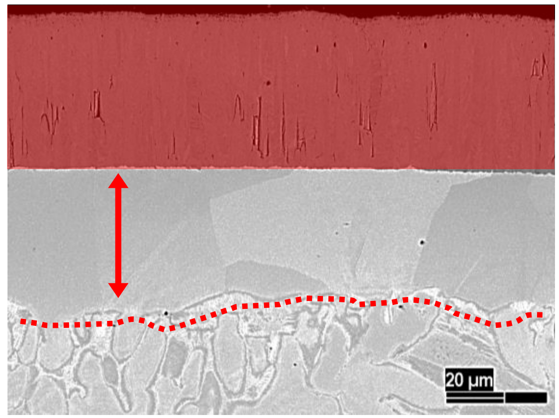


Cr/CrNi 9.8±0.3 µm
1200 ºC 400 s
- decrease oxide zone significantly **70%**
- decrease α-Zr(O) layer size **60%**

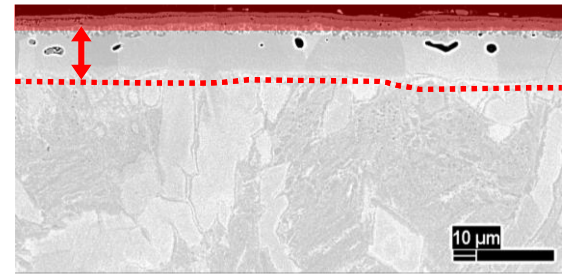
Cr/FeCrNi/Cr and Cr/CrNi/Cr



Uncoated E110
1200 ºC 400 s
- ZrO_2 50±5 µm
- α-Zr(O) 80±10 µm



Cr/FeCrNi 4.1±0.3 µm
1200 ºC 400 s
- slightly affect on oxide thickness **10%**
- decrease α-Zr(O) layer size **30%**
- make **α-Zr(O)|ex.β-Zr** interface smooth



Cr/CrNi 9.8±0.3 µm
1200 ºC 400 s
- decrease oxide zone significantly **70%**
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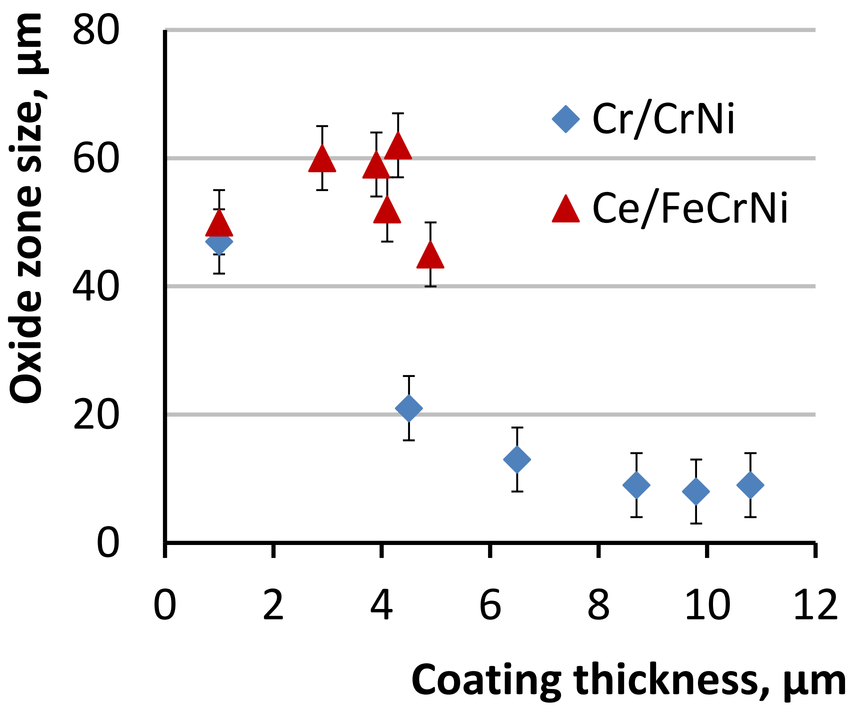
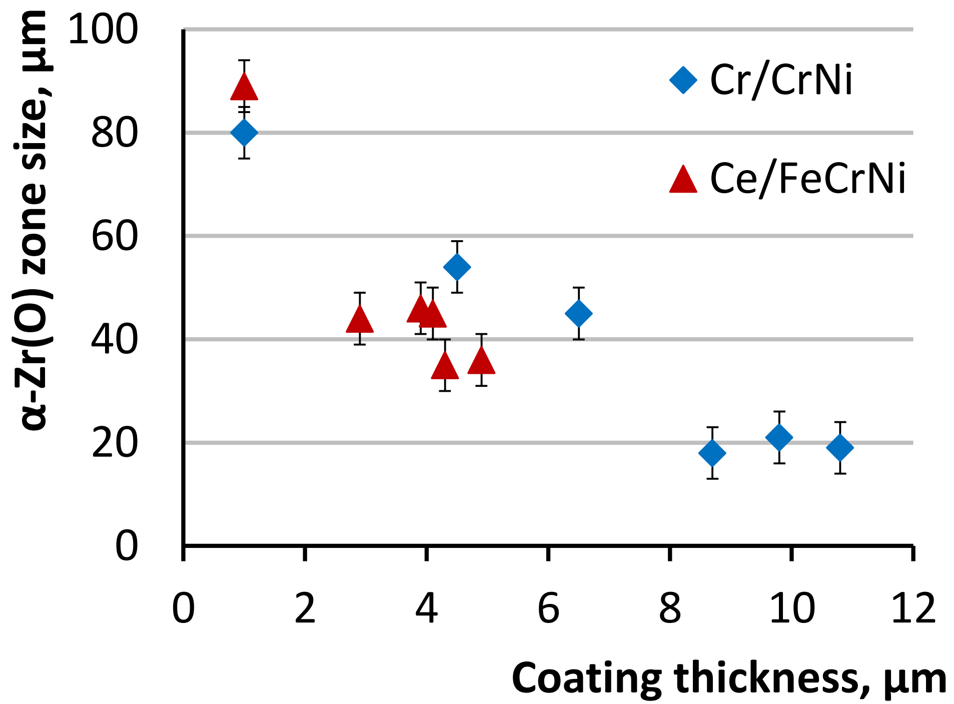
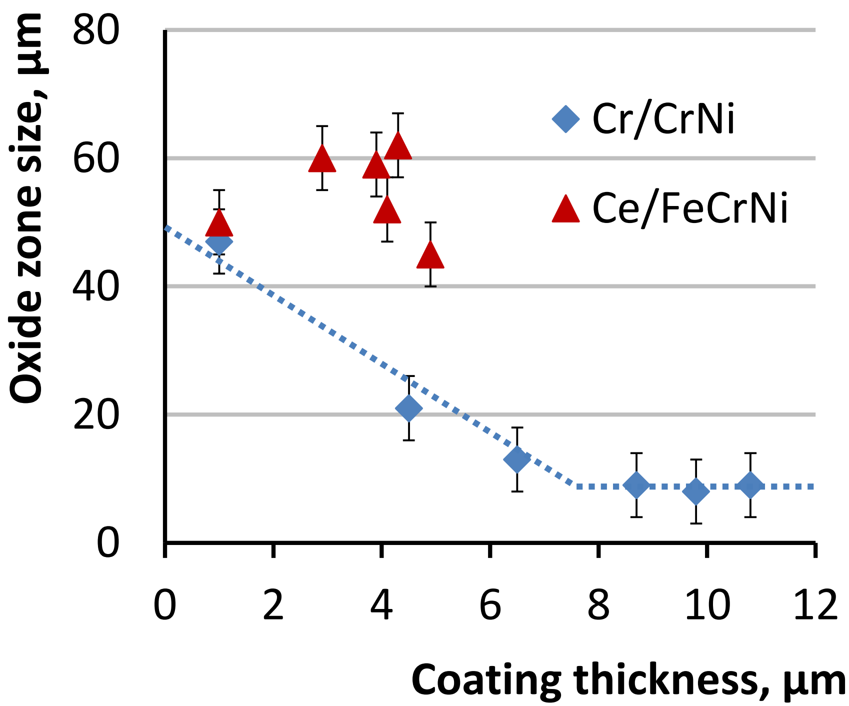
Coating thickness effect at 1200 ºC 400 s

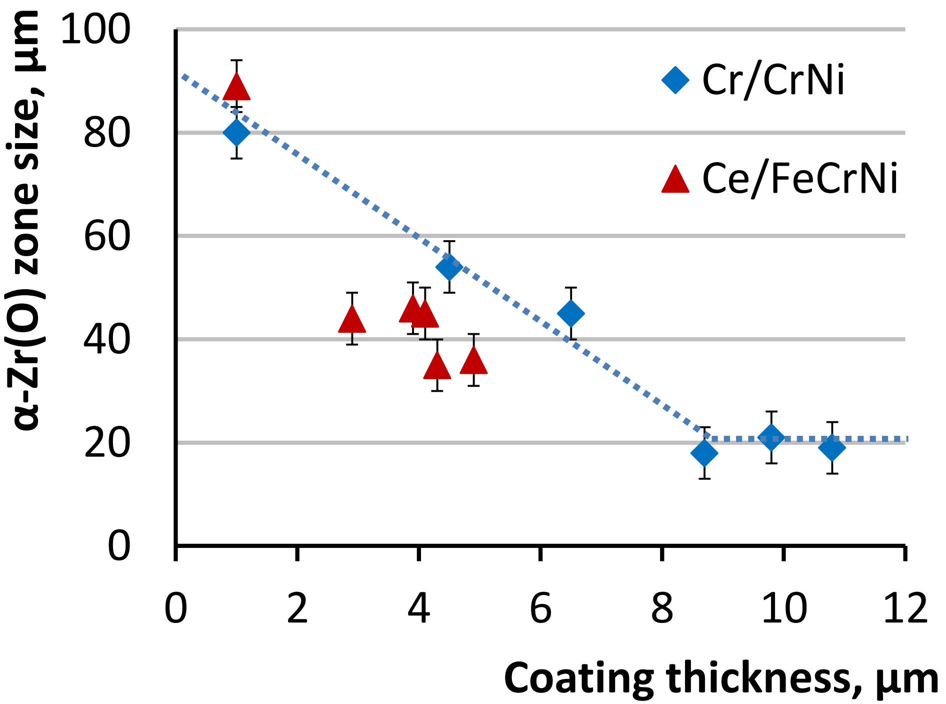




Value «oxide zone» on this figure include ZrO_2 layer and oxides formed at coatings deposited.

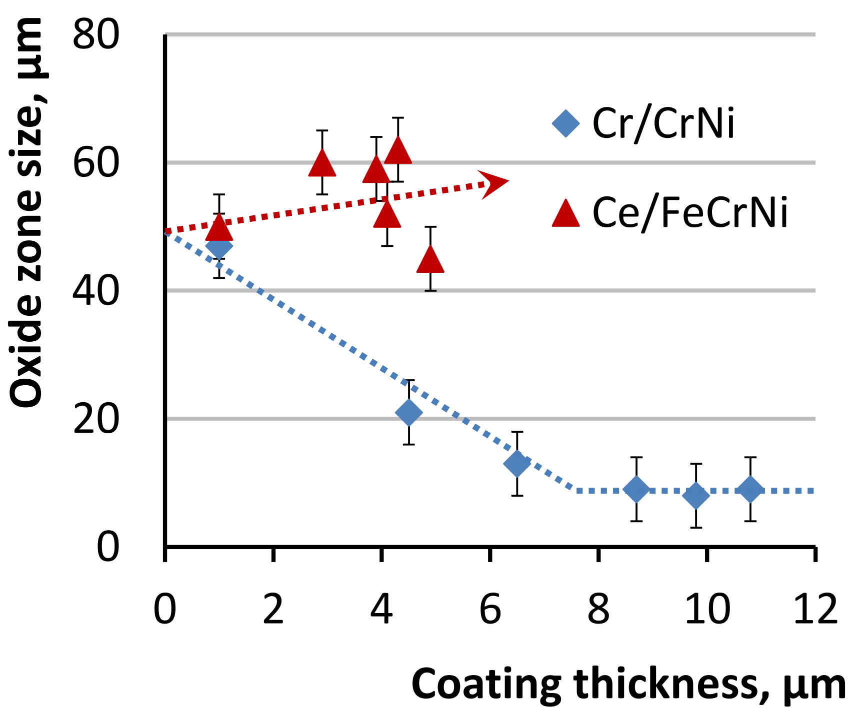
Coating thickness effect at 1200 ºC 400 s

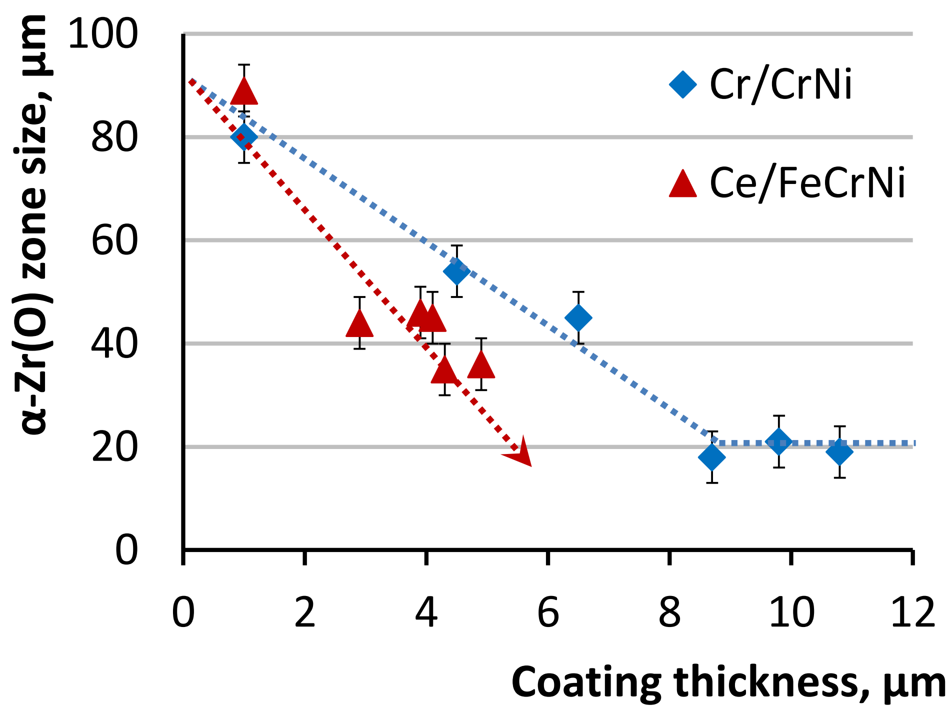




Oxygen penetration degree decreases with increasing Cr/CrNi coating thickness and saturates at about 8 µm (blue dotted lines).

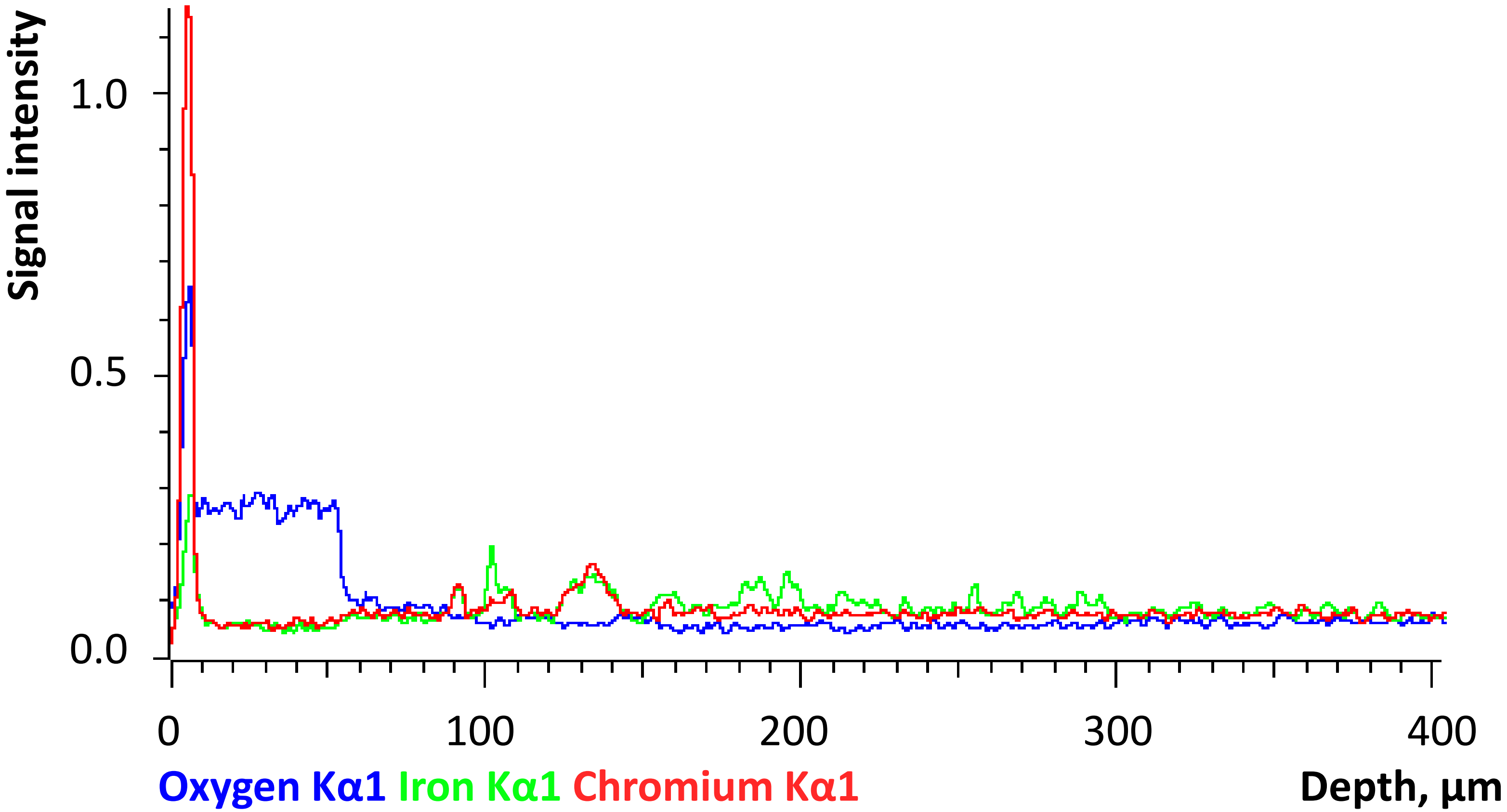
Coating thickness effect at 1200 ºC 400 s





Samples with Cr/FeCrNi coatings reveal higher oxide zone size, but lower size of α-Zr(O) zone (red dotted arrows).

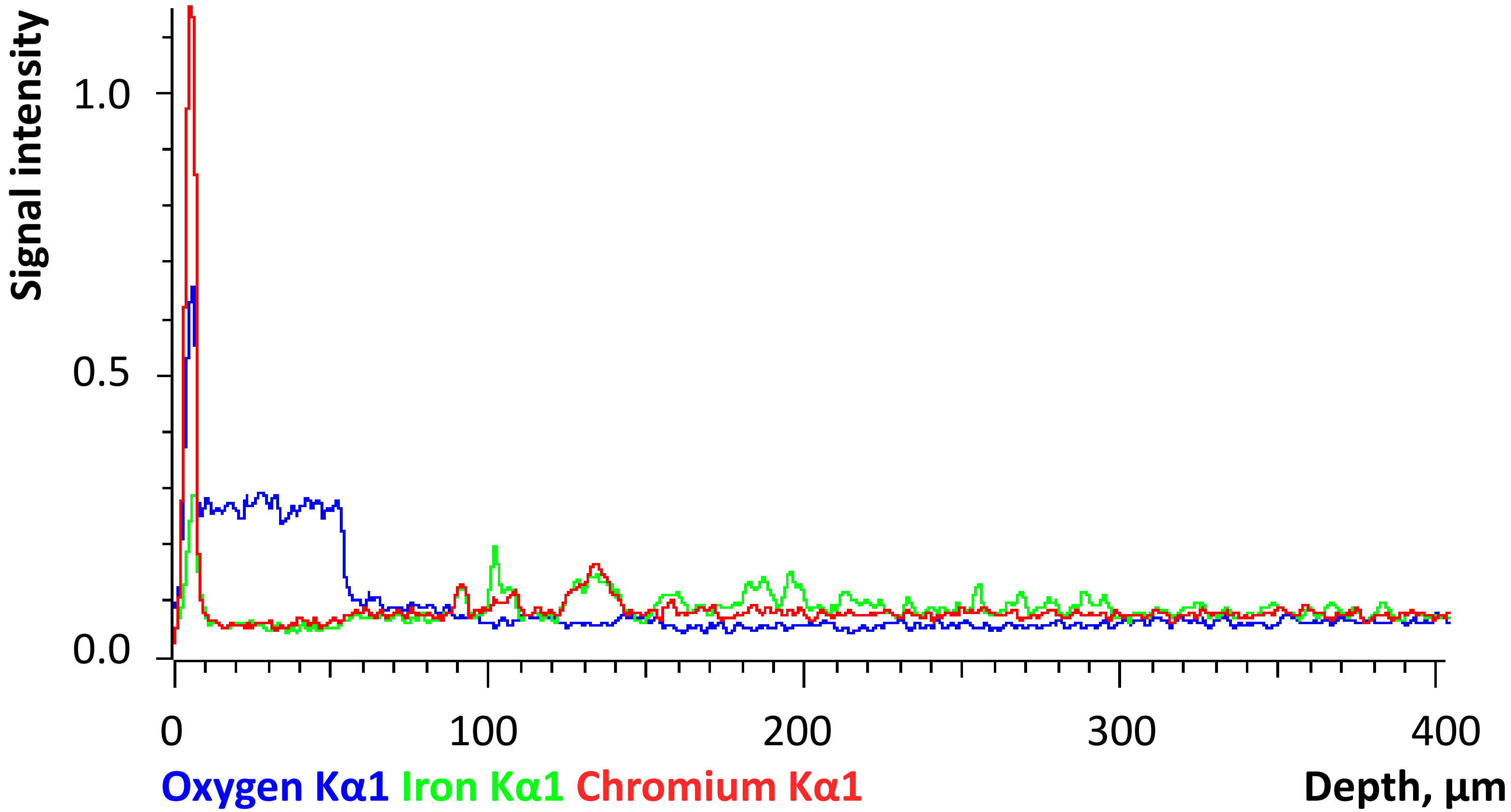
X-ray microanalysis



Data from sample with Cr/FeCrNi coating 4.1 µm thick after oxidation at 1200 ºC 400 s

X-ray microanalysis

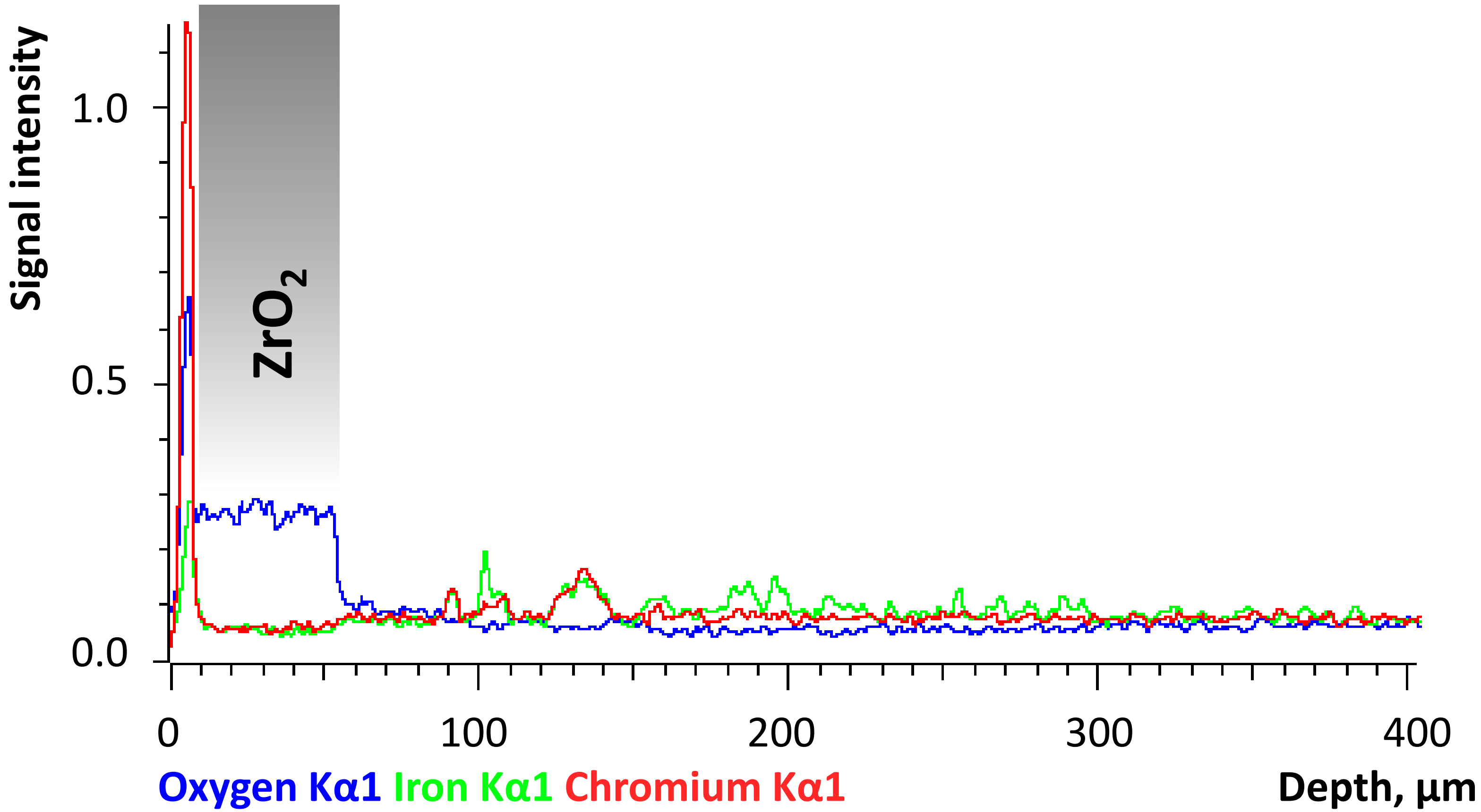
↓ Cr/FeCrNi coating oxidized



Data from sample with Cr/FeCrNi coating 4.1 µm thick after oxidation at 1200 ºC 400 s

X-ray microanalysis

↓ **Cr/FeCrNi** coating oxidized



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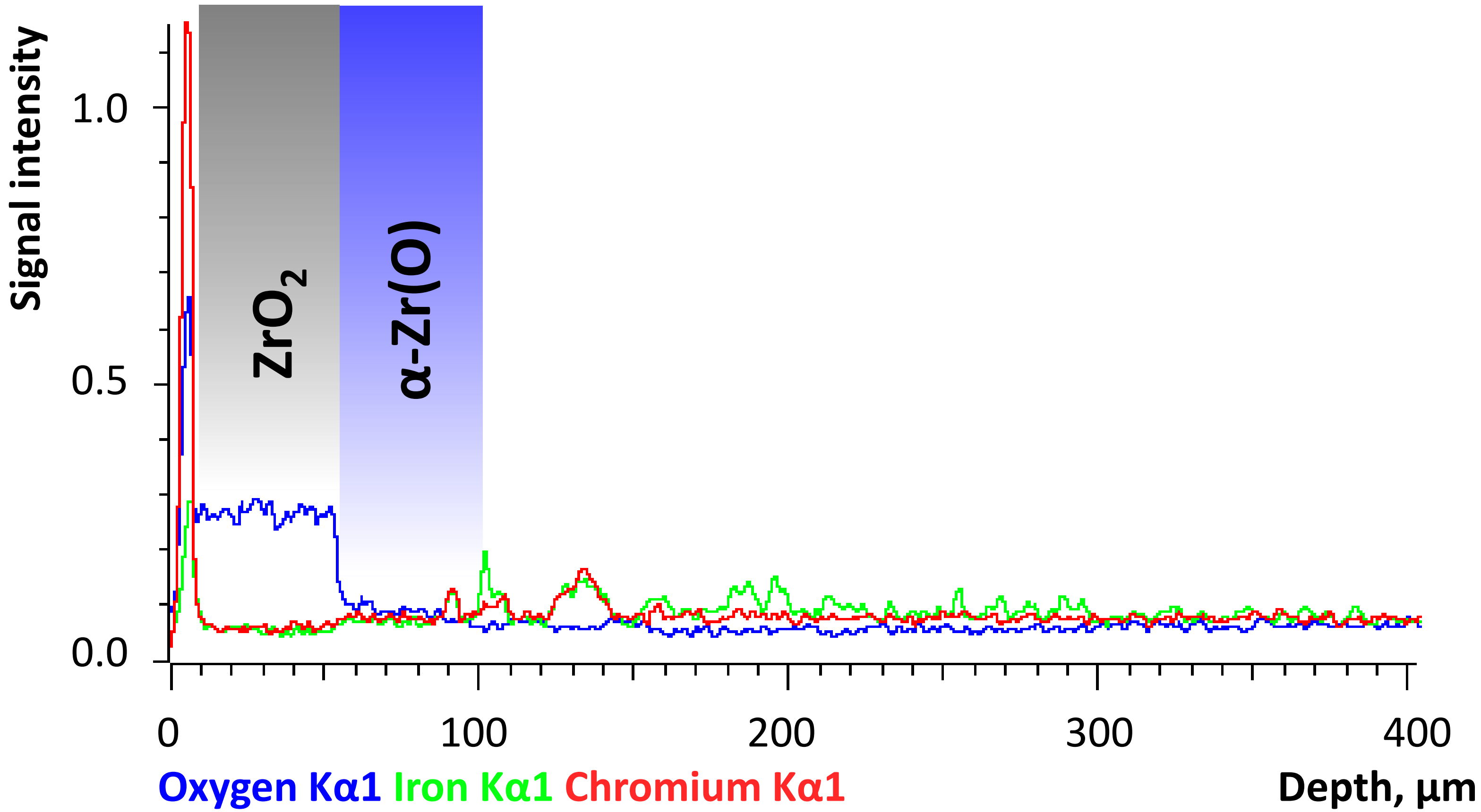

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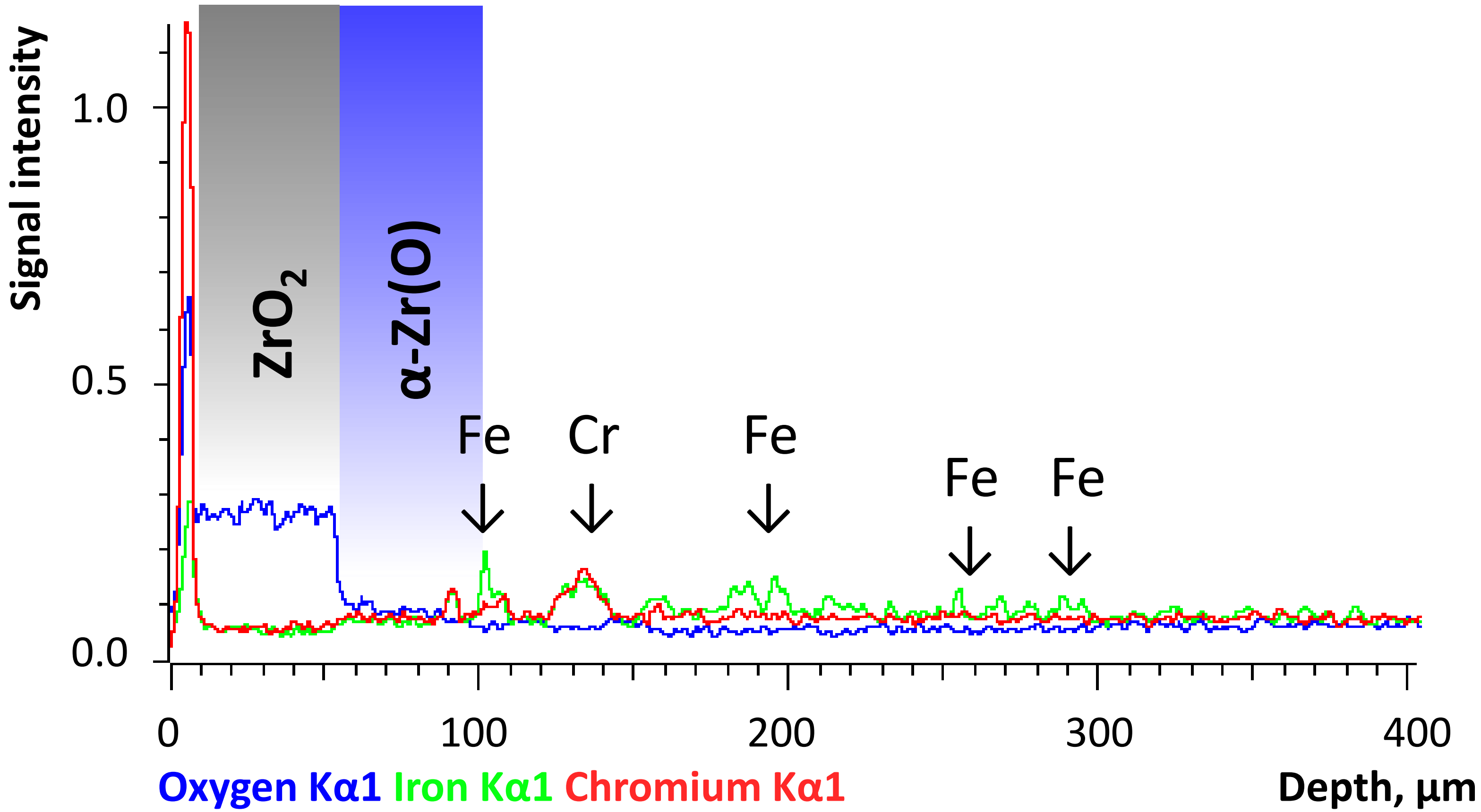

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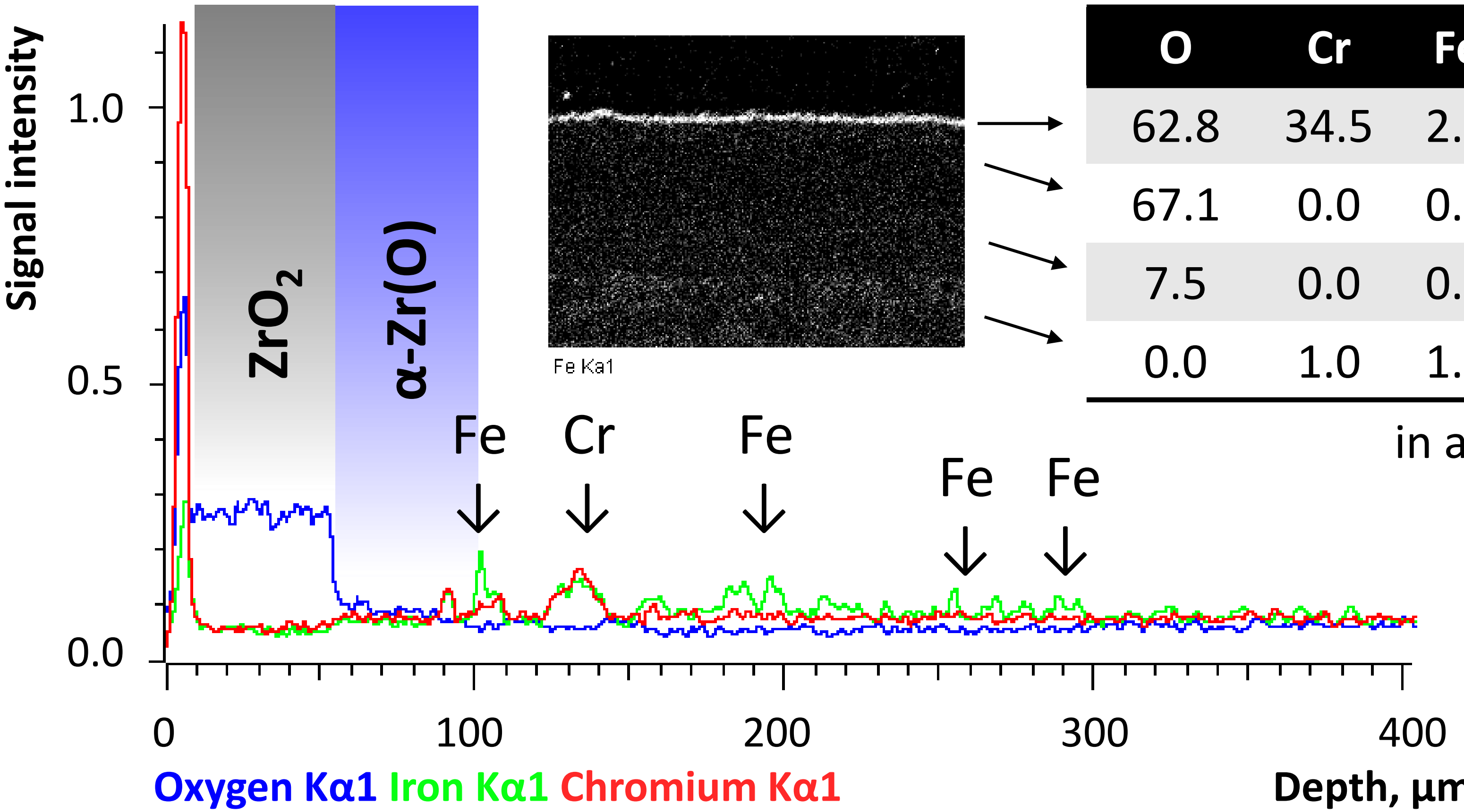
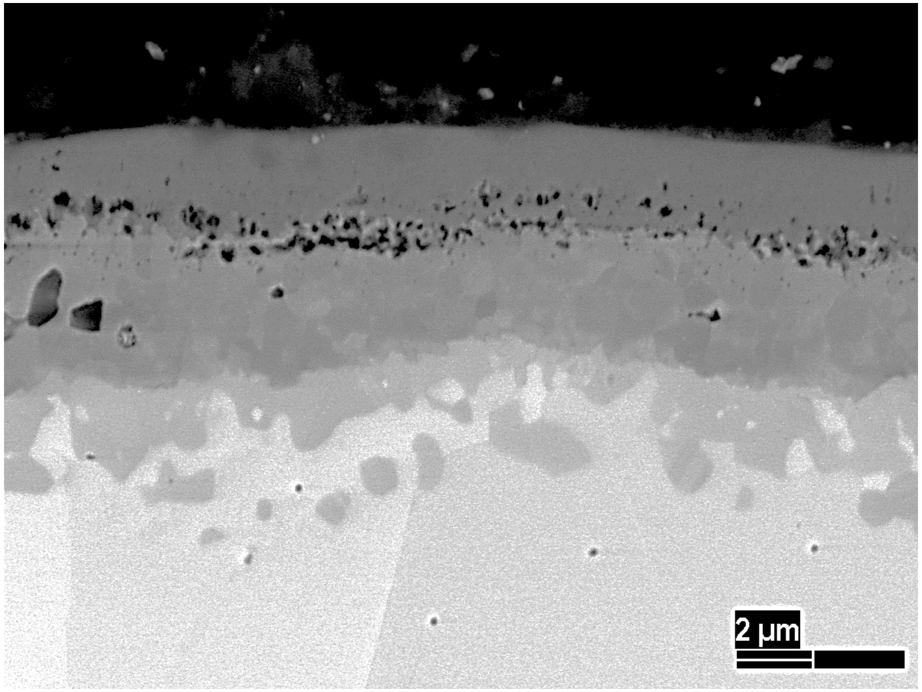


O	Cr	Fe	Zr
62.8	34.5	2.4	0.3
67.1	0.0	0.0	32.9
7.5	0.0	0.0	92.5
0.0	1.0	1.1	97.9

in atomic %

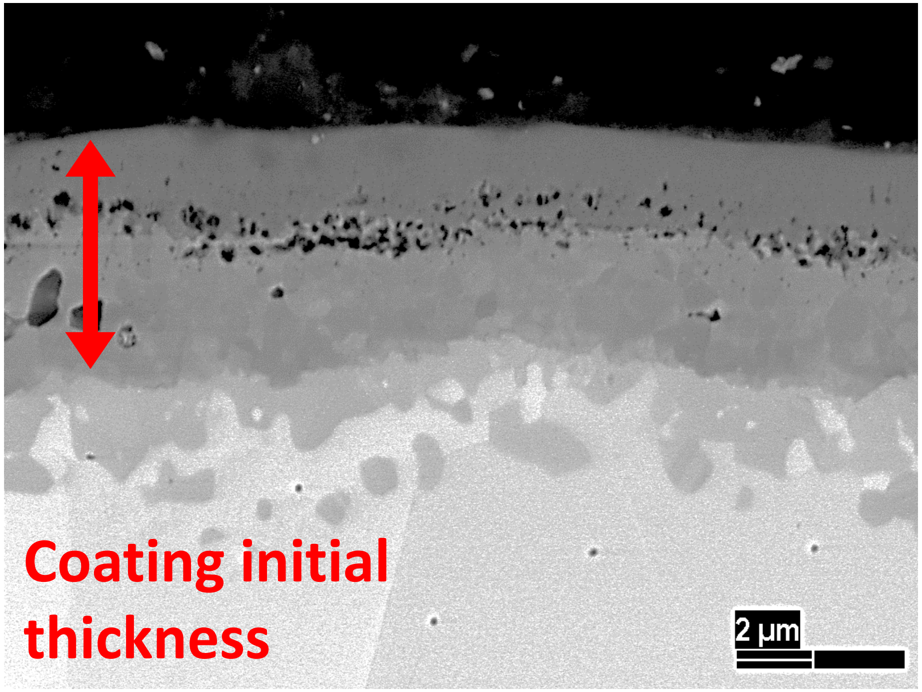
Data from sample with Cr/FeCrNi coating 4.1 µm thick after oxidation at 1200 ºC 400 s

Cr/CrNi coating cross section



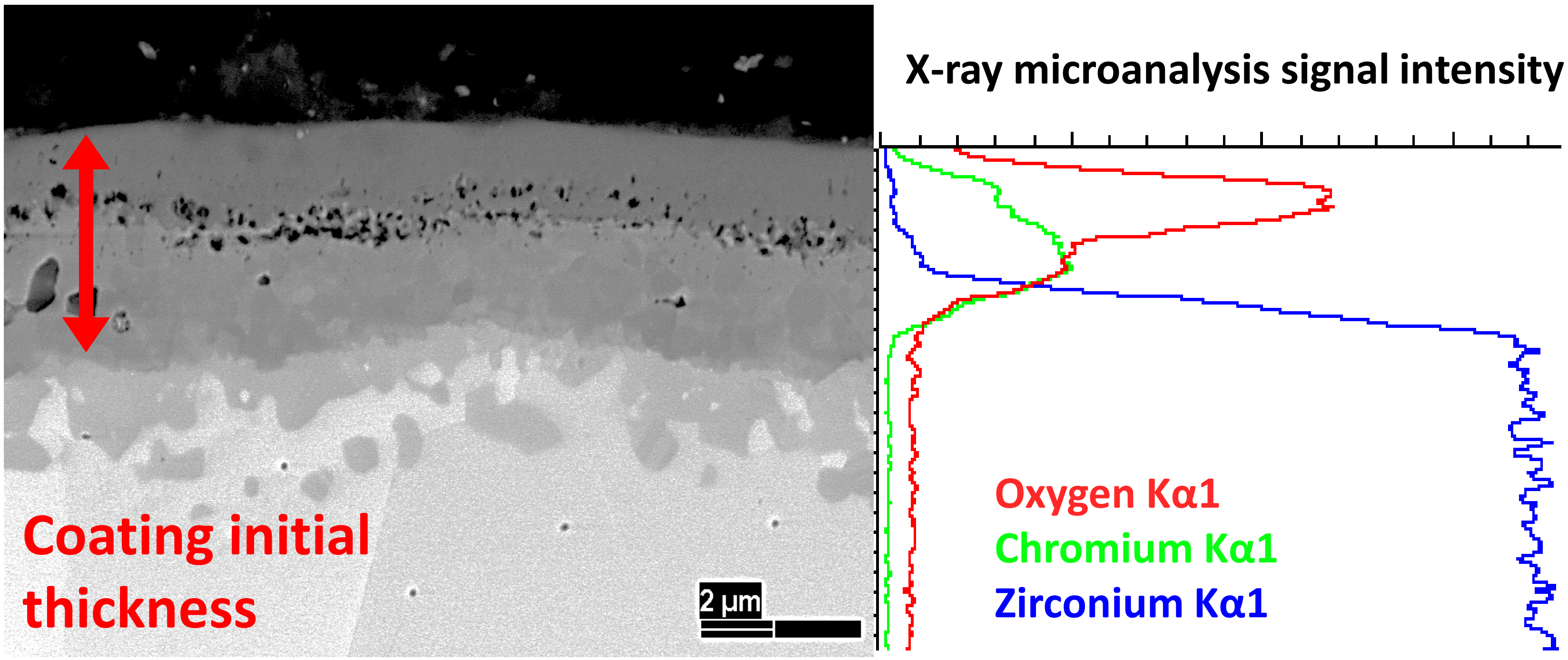
Multilayer structure of oxidized Cr/CrNi coating is observed (oxidation at 1200 ºC 400 s)

Cr/CrNi coating cross section



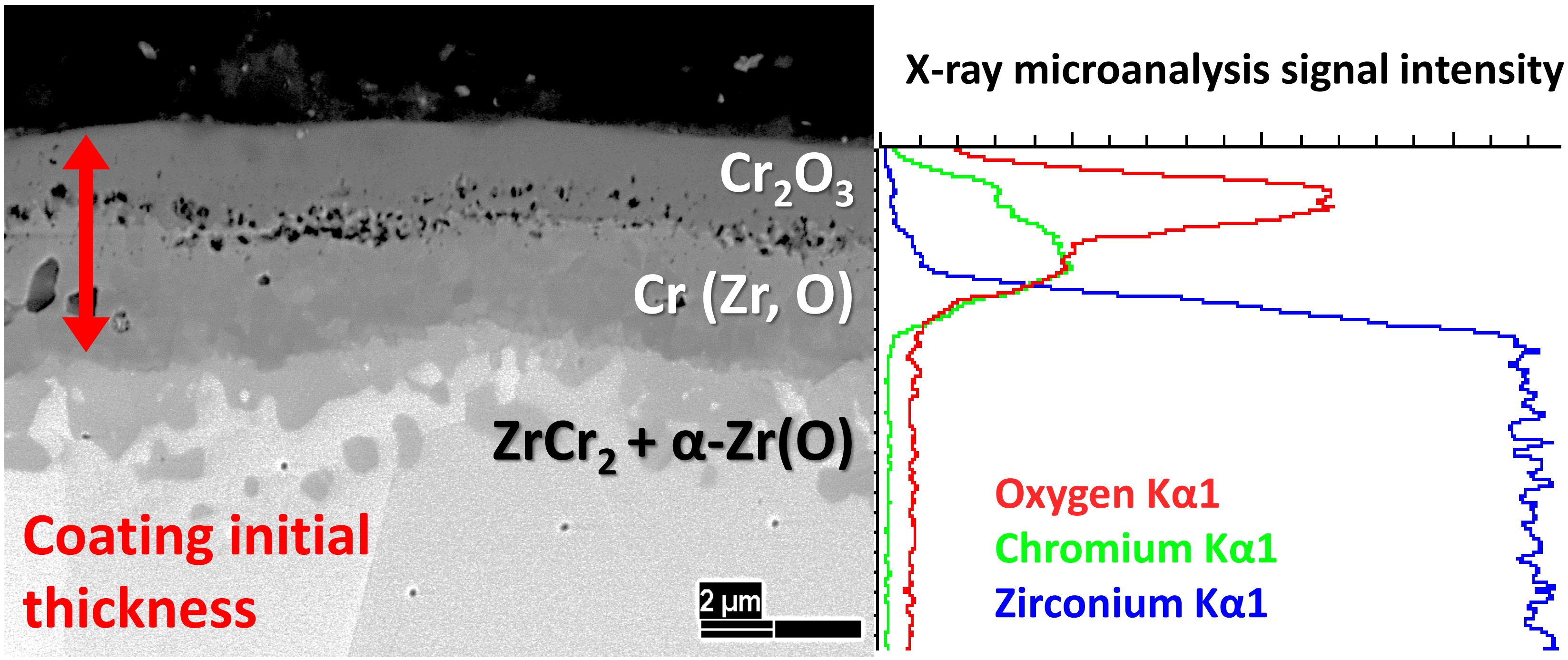
Multilayer structure of oxidized Cr/CrNi coating is observed (oxidation at 1200 ºC 400 s)

Cr/CrNi coating cross section



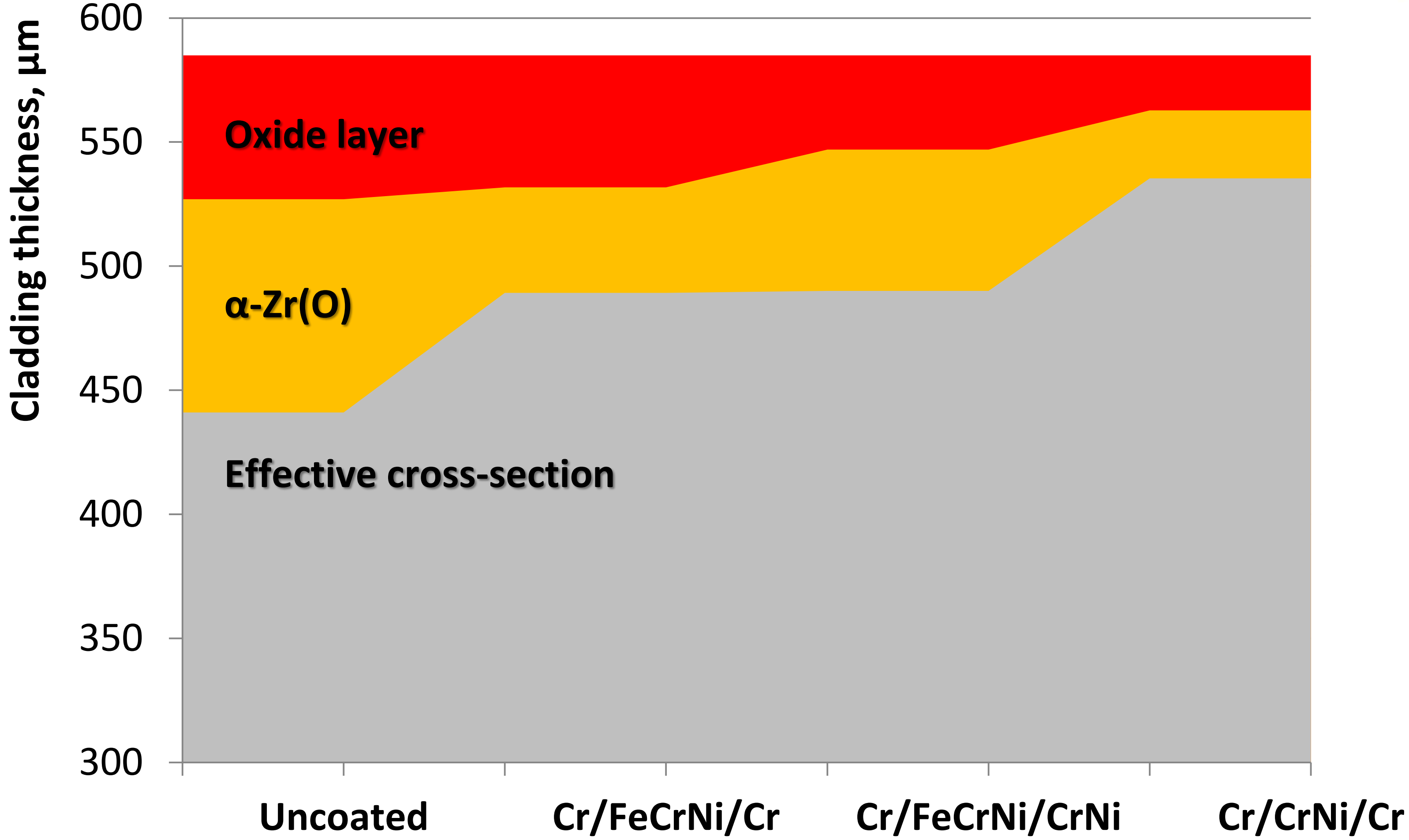
Multilayer structure of oxidized Cr/CrNi coating is observed (oxidation at 1200 ºC 400 s)

Cr/CrNi coating cross section



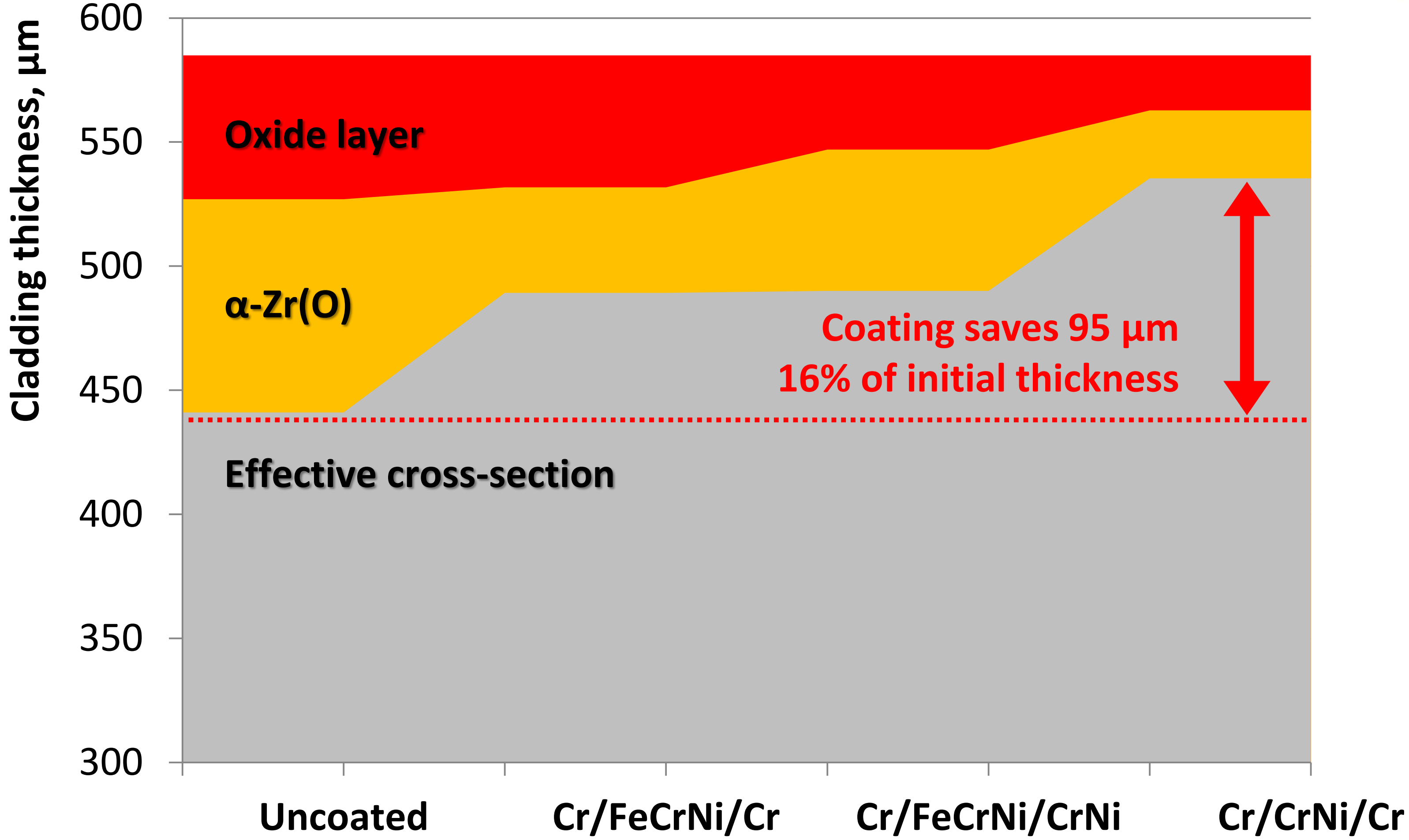
It is observed that **diffusion greatly affect** coatings evolution during oxidation at 1200 ºC

Effective cladding cross section



Oxidation at 1200 ºC 400 s

Effective cladding cross section



Oxidation at 1200 ºC 400 s

Conclusion

1. Experimental results on the high-temperature oxidation of fuel claddings fragments from E110 alloy with FeCrNi and CrNi based multilayer coatings 1.0-10.0 µm thick were obtain;
2. It is shown that **microcracks** arises in Cr-coatings during oxidation at 800 ºC presumably caused by internal stresses α-β transformation in Zr may lead to coatings destruction and increase corrosion;
3. It is established that Fe and Cr atoms migrate from coatings to α-Zr(O) | ex. β-Zr interface during high-temperature oxidation, that presumably control oxygen penetration into the bulk metal;
4. It is shown that diffusion fast rate leads to coatings stratification during high-temperature oxidation;
5. As observed, Cr/FeCrNi/Cr and Cr/CrNi/Cr coatings deposited reduce total oxygen penetration depth by **34%** and **66%** respectively during oxidation at 1200 ºC, save up to **95 µm** of cladding material.

Thank you for attention!