Effect of chromium grain size and morphology on the HT oxidation behavior of chromium coated Zr based alloys

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EFFECT OF CHROMIUM GRAIN SIZE AND MORPHOLOGY ON HIGH TEMPERATURE STEAM OXIDATION BEHAVIOR OF CHROMIUM COATED Zr BASED ALLOYS

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Context: **Chromium coated zirconium** based nuclear fuel claddings are developed and studied within the CEA-Framatome-EDF joint research program as **"Enhanced Accident Tolerant Fuel" (EATF)** cladding short-term concept for nuclear light water reactors [1] [2].

Objective: To investigate the influence of the initial chromium grain size and morphology on the High Temperature (HT) steam oxidation behavior of 6-8µm thick Cr-coated zirconium based specimens, by coupling several *post-mortem* experimental techniques, that is, FEG-SEM-EBSD, Glow discharge Mass Spectrometry (GDMS), Electron Probe Micro Analysis (EPMA) and Raman spectroscopy.

Materials and experimental conditions:

- ✓ **Zr based alloys: Sheets specimens (thickness ~1.2 mm)**
  Tubular cladding geometry (thickness ~0.6 mm)
- ✓ **6-8 µm thick chromium coatings** deposited by a special Physical Vapor Deposition (PVD) process:
  => very good bonding with the Zr substrate - dense coating without apparent porosity - good thickness homogeneity

Experimental conditions:

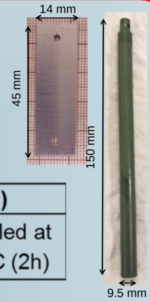
1- Pre-annealing thermal treatments – 2h at 700 and 800°C, under vacuum

2- HT steam oxidation at 1200°C in steam and final water quenching (using reference CEA "DEZIROX" facility [3])

	(1)	(2)	(3)
Samples	Virgin	Annealed at 700 °C (2h)	Annealed at 800 °C (2h)

Post-mortem measurements:

- ❑ Weight gains and Post-Quenching (PQ) examination/analysis: FEG-SEM-EBSD, GDMS, EPMA and Raman spectroscopy



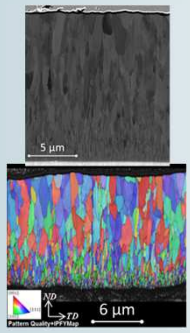
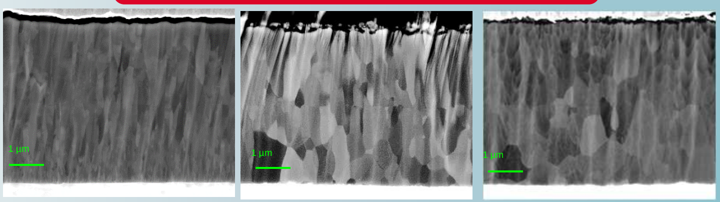


Fig. 1 : Typical µsctructures of Cr coating on Zr substrate (a- FEG-SEM micrograph; b- EBSD map)

Pre-annealing thermal treatment



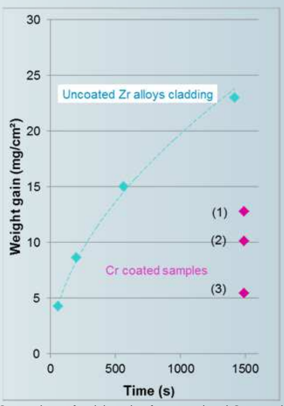
As deposited | Annealed sample at 700°C (2h) | Annealed sample at 800°C (2h)

(SEM-BSE micrographs of the outer chromium coating)

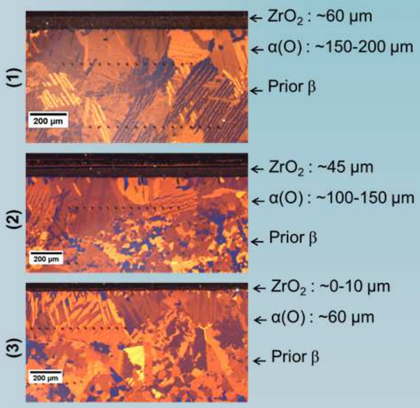
During the annealing treatment, the Cr coating experienced recrystallization:

➡ Initial columnar grains morphology became more equiaxed

HT oxidation and PQ microstructures



Comparison of weight gain of uncoated and Cr coated Zr alloys cladding after HT oxidation



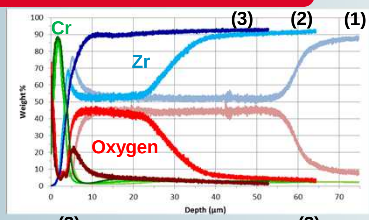
➡ Weight gains of pre-annealed Cr-coated specimen lower than non-annealed ones

➡ Significant decrease of ZrO_2 and α (O) thicknesses for pre-annealed samples

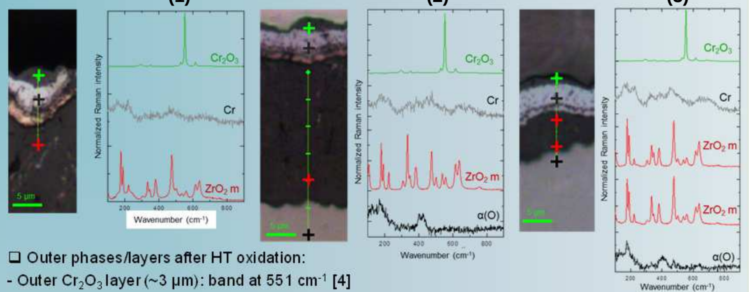
PQ microstructures and oxygen diffusion

➡ Glow dischage mass spectrometry measurements

- ✓ Interdiffusion between Cr and Zr
- ✓ Decrease of oxygen diffusion into the Zr substrate for pre-annealed samples



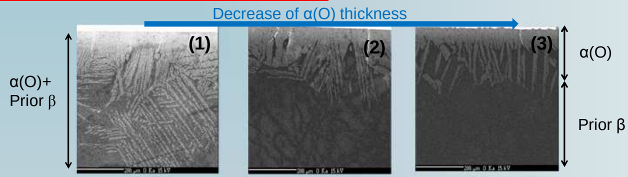
Cr_2O_3, Cr and ZrO_2 layers:



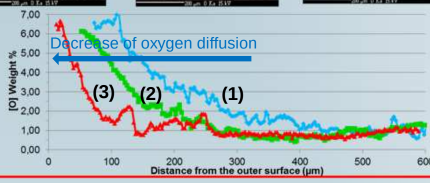
- ❑ Outer phases/layers after HT oxidation:
- Outer Cr_2O_3 layer (~3 µm): band at 551 cm^{-1} [4]
- Residual (non oxidized) metallic Cr
- Monoclinic Zirconia (prior-quadratic phase retransformed to monoclinic one upon final quenching)

Raman spectroscopy measurements

Metallic Zr substrate , α (O) and Prior-β:



EPMA Oxygen diffusion profiles measured from the ZrO_2/α(O) interface



Conclusions and on-going/further work

- Thermal pre-annealing treatment results in an increase of Cr size grains before the HT oxidation
- ➢ Weight gains of pre-annealed Cr-coated specimen were lower than the non-annealed ones.
- ➢ Thickness of ZrO_2 and αZr(O) phases were significantly reduced for the pre-annealed samples, indicating that the grain size and morphological evolutions of the chromium coating upon the pre-annealing thermal treatment may influence its further HT oxidation behavior, thus inducing:
  - Overall, higher resistance to HT oxydation
  - Significant delay in the oxygen ingress into the Zr based substrate
- On-going: complementary EBSD, TEM... analysis for more detailed informations on the associated oxygen diffusion mechanisms...

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Some references:

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