# OECD NEA EGATFL
# Coatings sub-Task Force

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E N G I N E E R I N G A T I L L I N O I S


US DOE NEUP IRP—UIUC (ATF) & UT ($C^3$)

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

UIUC

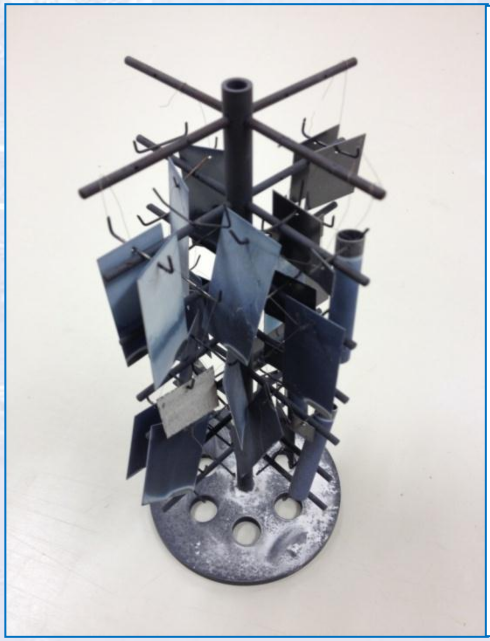
- Magnetron sputtering of FeCrAl on Zircaloy 2
- 700 ºC steam Δm
- Dynamic autoclave Δm (BWR-NWC, 288 ºC, 48 hrs.)
- AES, XRD, STEM, SEM, EDS

UT

- Cathodic arc PVD of MAX (TiAlN) phases on ZIRLO
- Static autoclave Δm (360 ºC, pure $H_2O$, several days)
- Optical microscopy, SEM, XRD

# UT Work

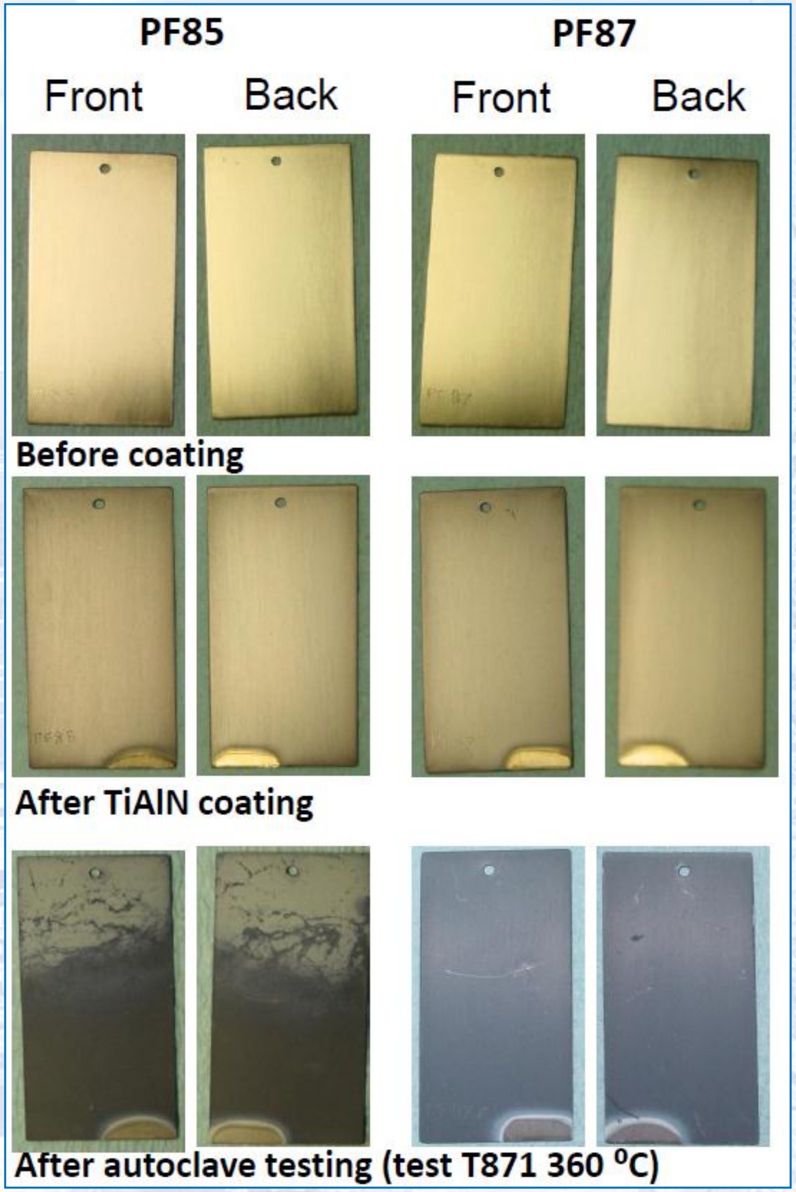
- 6 generations of MAX phase coatings
- Static autoclave 360 ºC Δm
- 500 ºC SCW, 800 ºC steam beginning
- TiAlN (350 ºC cathodic arc, →20 μm) and $Ti_3AlC_2$ (400 ºC magnetron sputtering, →3 μm)

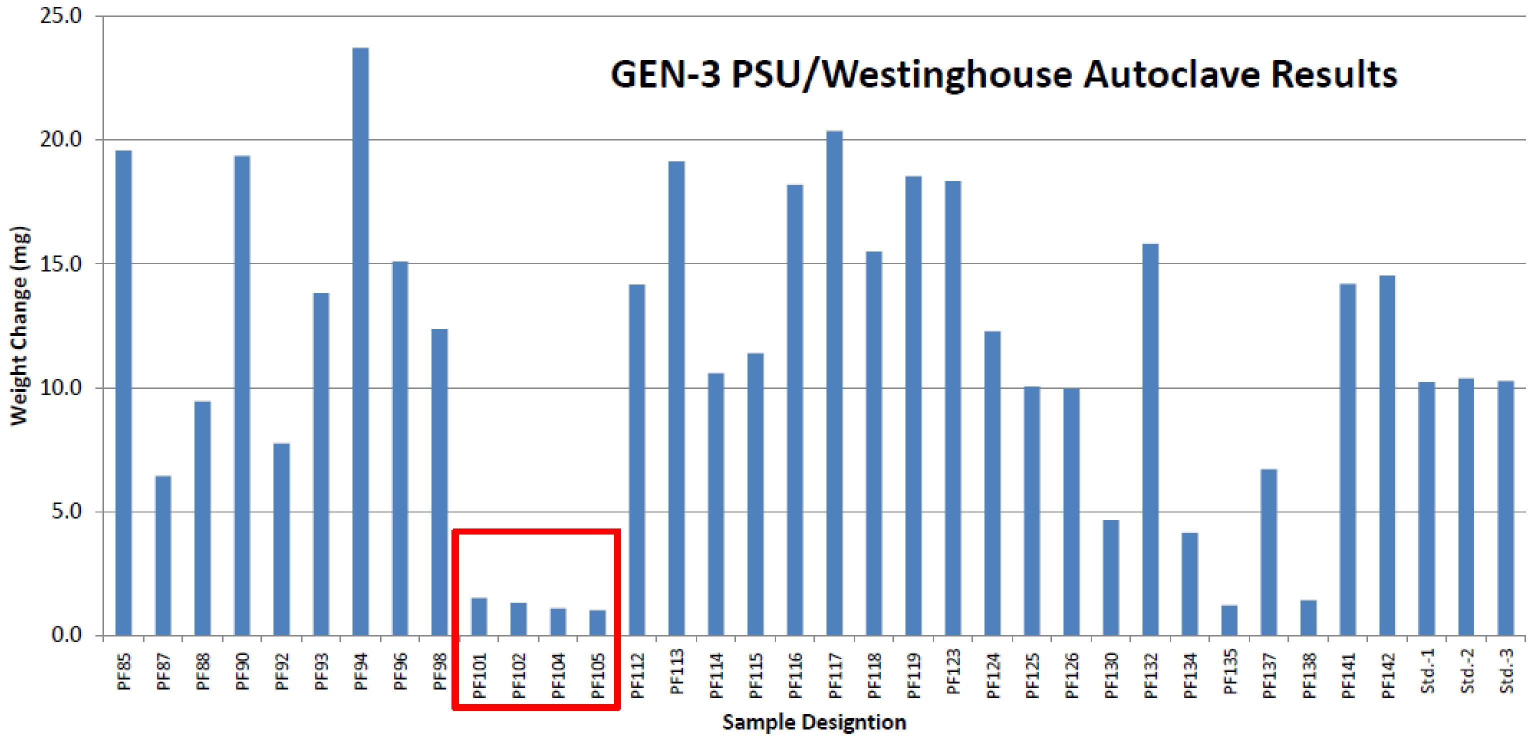


- Gen 1 coating (June 2013)
  - 3 days in 360ºC, static pure water
- Gen 2 coating (July 2013)
  - 3 days in 360ºC, static pure water
- Gen 3 coating (September 2013)
  - 3 days in 360ºC, static pure water
- Gen 4 coating (November 2013)
  - 7/21/39.8/53.8/67.8 days in 360ºC static pure water
- Gen 5 coating (February 2014)
  - 14/32.8/46.8/60.8 days in 360ºC static pure water

# Generation 3

| # | Description |
|---|---|
| 1 | TiAlN / Ti BC (10 µin Ra) coated zirlo; heat treated: 350°C, 4 hrs, $N_2$ |
| 2 | TiAlN / Ti BC (10 µin Ra) coated zirlo; heat treated: 350°C, 4 hrs, $N_2$ |
| 3 | TiAlN / Ti BC (10 µin Ra) coated zirlo; heat treated: 500°C, 4 hrs, $N_2$ |
| 4 | TiAlN / Ti BC (10 µin Ra) coated zirlo; heat treated: 500°C, 4 hrs, $N_2$ |
| 5 | TiAlN / Ti BC (10 µin Ra) coated zirlo |
| | |
| 6 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 1 minute ion pre-heat |
| 7 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 1 minute ion pre-heat |
| 8 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 1 minute ion pre-heat |
| 9 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 1 minute ion pre-heat |
| | |
| 10 | TiN / Ti BC (10 µin Ra) coated zirlo |
| 11 | TiN / Ti BC (10 µin Ra) coated zirlo |
| 12 | TiN / Ti BC (10 µin Ra) coated zirlo |
| 13 | TiN / Ti BC (10 µin Ra) coated zirlo |
| | |
| 14 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 5 minute ion pre-heat |
| 15 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 5 minute ion pre-heat |
| 16 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 5 minute ion pre-heat |
| 17 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 5 minute ion pre-heat |
| 18 | TiAlN / Ti BC (10 µin Ra) coated zirlo; 5 minute ion pre-heat |
| | |
| 19 | TiAlN / Ti BC (10 µin Ra) coated zirlo; slightly increased $N_2$ pressure |
| 20 | TiAlN / Ti BC (10 µin Ra) coated zirlo; slightly increased $N_2$ pressure |
| 21 | TiAlN / Ti BC (10 µin Ra) coated zirlo; slightly increased $N_2$ pressure |
| 22 | TiAlN / Ti BC (10 µin Ra) coated zirlo; slightly increased $N_2$ pressure |
| 23 | TiAlN / Ti BC (10 µin Ra) coated zirlo; slightly increased $N_2$ pressure |
| | |
| 24 | TiAlN / Ti BC (10 µin Ra) coated zirlo; increased substrate bias to 100 Volts |
| 25 | TiAlN / Ti BC (10 µin Ra) coated zirlo; increased substrate bias to 100 Volts |
| 26 | TiAlN / Ti BC (10 µin Ra) coated zirlo; increased substrate bias to 100 Volts |
| 27 | TiAlN / Ti BC (10 µin Ra) coated zirlo; increased substrate bias to 100 Volts |
| | |
| 28 | TiAlN / Ti BC (10 µin Ra) coated zirlo; higher $N_2$ pressure; reduced source voltage |
| 29 | TiAlN / Ti BC (10 µin Ra) coated zirlo; higher $N_2$ pressure; reduced source voltage |
| 30 | TiAlN / Ti BC (10 µin Ra) coated zirlo; higher $N_2$ pressure; reduced source voltage |
| 31 | TiAlN / Ti BC (10 µin Ra) coated zirlo; higher $N_2$ pressure; reduced source voltage |
| | |
| 32 | Uncoated zirlo, 10 µin Ra finish. |
| 33 | Uncoated zirlo, 10 µin Ra finish. |

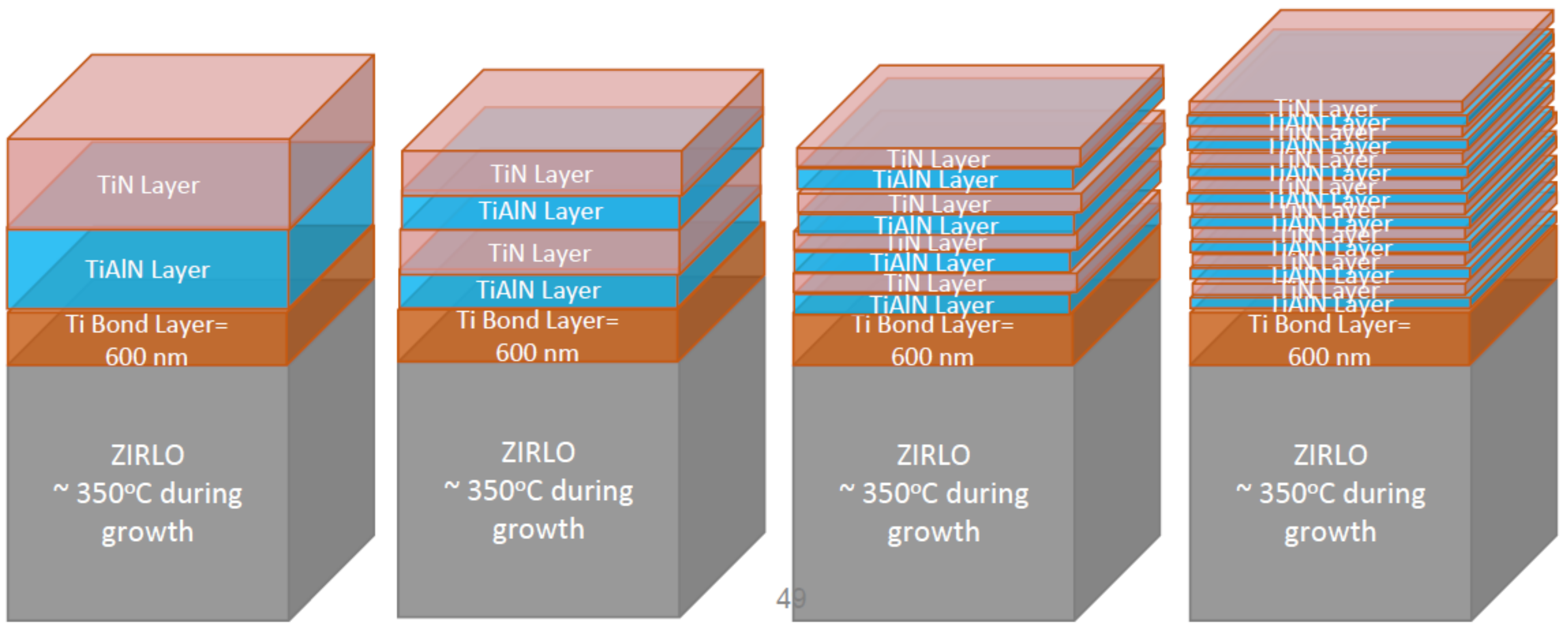




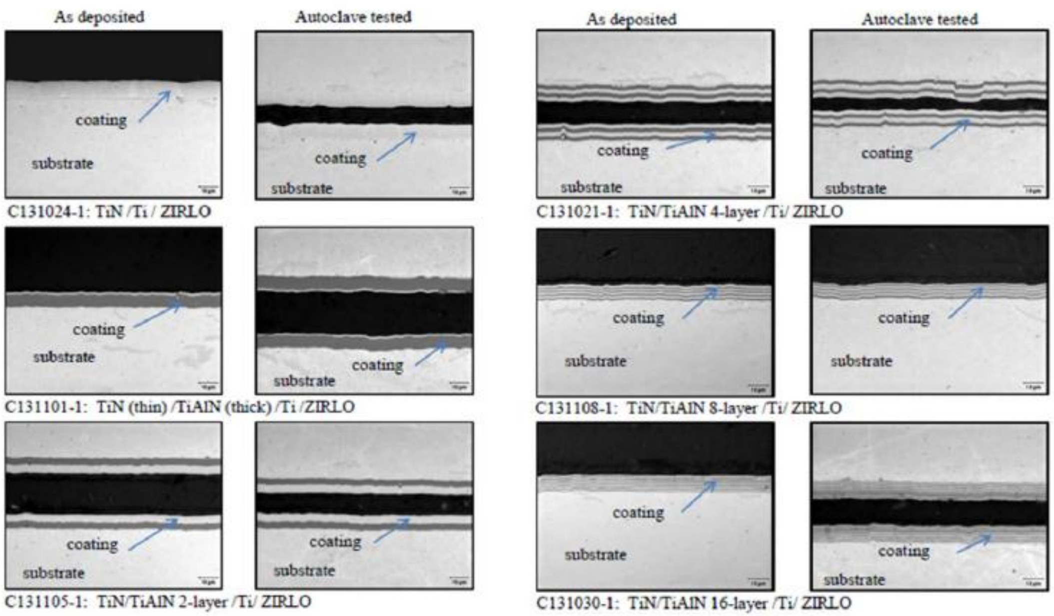

**Limited weight gain was observed for the TiN coatings (suggesting good resistance to oxidation evaluated by the autoclave test)**

# Generation 4

- Longer corrosion Testing (November 2013)
- 7/21/39.8/53.8/67.8 days in 360°C, static pure water
- Use multi-layer architecture
- Check optimum coating thickness 2-4-8-16 microns
- Use TiN outer layer to stop Al egress



# Generation 4




**No significant oxidation**

**No aluminum diffusion/depletion**

**No degradation of ZIRLO**

**TiN layer enhanced the coating performance by reducing/eliminating the aluminum diffusion through the coating.**

**Therefore, a very thin (0.5-2 micron) outer TiN layer or less should be sufficient to protect the underlying TiAlN coatings.**

# Generation 4

- Weight gain was minimal for all samples, about an order of magnitude improvement over an uncoated ZIRLO sample.
- The overall layer thickness should be kept low to avoid stress accumulation.
- The presence of a very thin layer of TiN was enough to stop reaction with steam.
- Corrosion testing continues now to longer times.

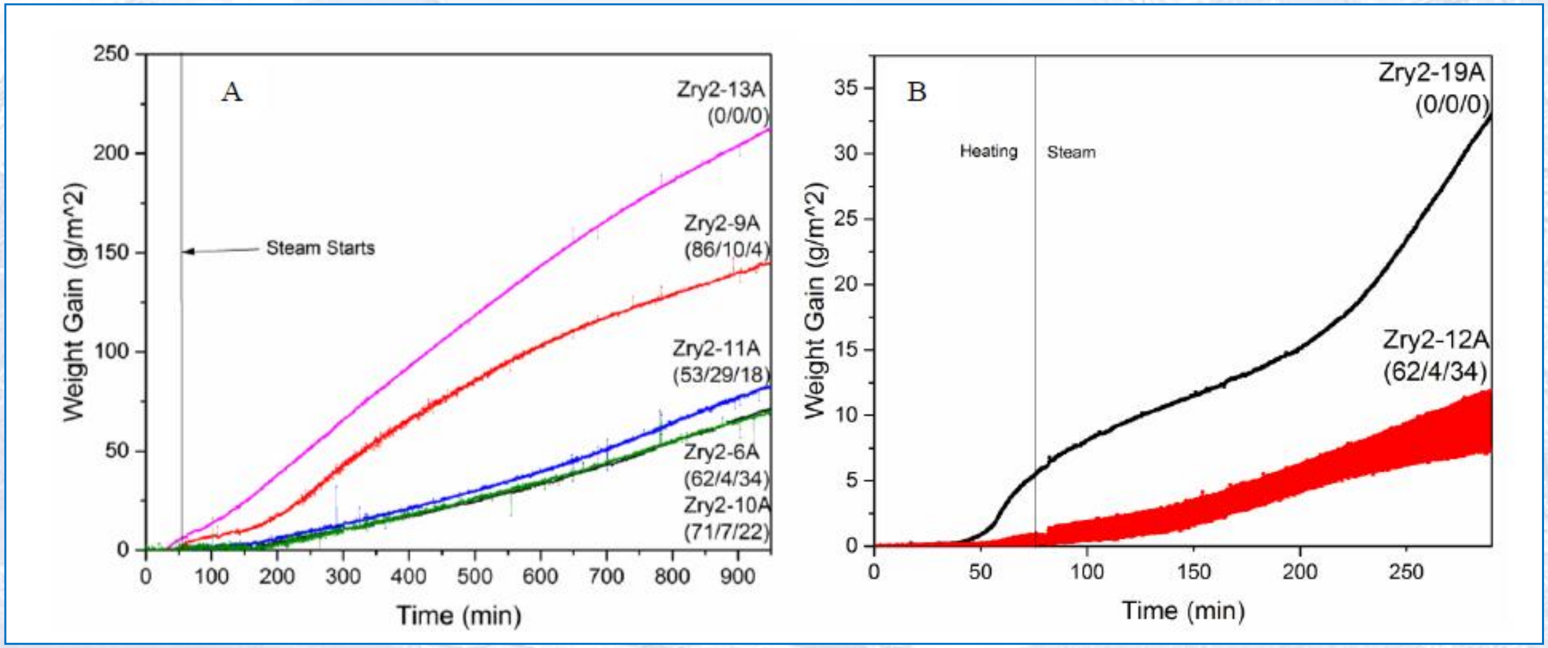
# UIUC Work

- FeCrAl various compositions via magnetron sputtering on Zircaloy 2 and YSZ
- Thickness range 0.5→1.5 μm
- 700, 1100, 1250 ºC steam, BWR-NWC exposure
- Several microanalytical analysis techniques

Table 1. Sample identification matrix showing sputter growth conditions, exposure conditions, and microanalytical analysis techniques employed.

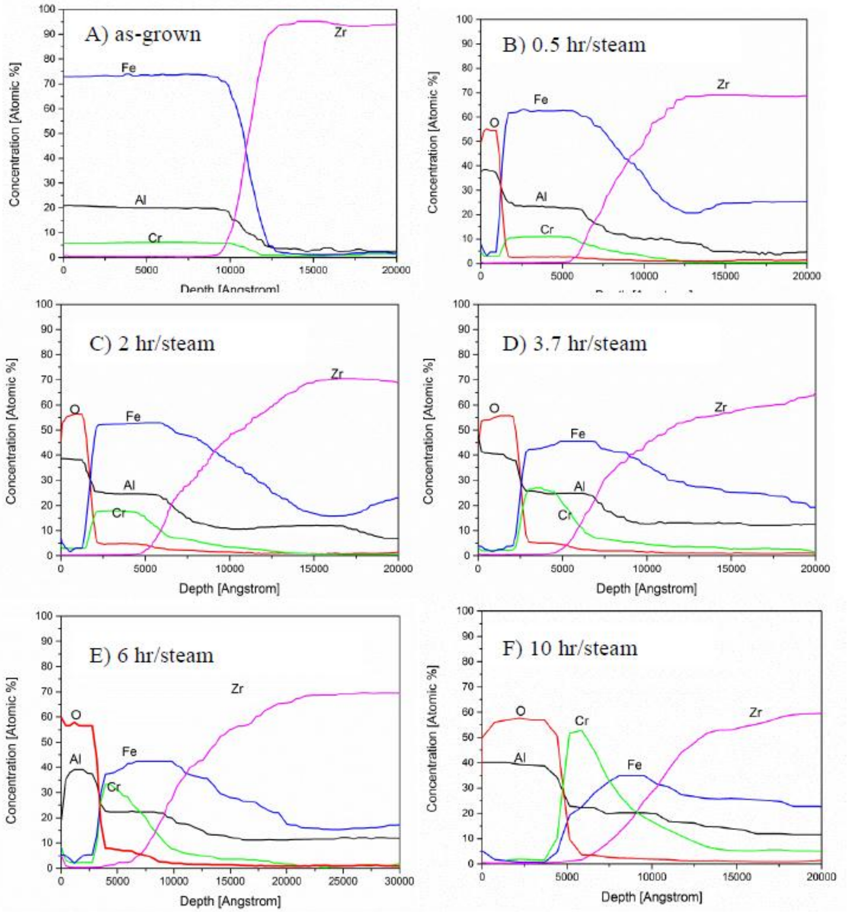
| Sample | [Fe/Cr/Al] | x [nm] | P/V/I [W/V/A] | Exposure Environment Phase | T [˚C] | t [hr] | Analysis Techniques |
|---|---|---|---|---|---|---|---|
| Zry2-6A | 62/4/34 | 600 | 80/377/0.2 | steam | 700 | 15 | STA, SEM, AES |
| Zry2-7A | 62/4/34 | 300 | 90/450/0.2 | steam | 700 | 10 | STA, STEM/EDS, AES |
| Zry2-9A | 86/10/4 | 300 | 71/355/0.2 | steam | 700 | 15 | STA, SEM, AES |
| Zry2-10A | 71/7/22 | 600 | 70/350/0.2 | steam | 700 | 15 | STA, SEM, AES |
| Zr2-11A | 53/29/18 | 300 | 70/350/0.2 | steam | 700 | 15 | STA, SEM/EDS, AES, XRD |
| Zry2-12A | 62/4/34 | 900 | 110/367/0.3 | steam | 700 | 3.7 | STA, SEM/EDS, AES, XRD |
| Zry2-13A | Uncoated | ----- | ----- | steam | 700 | 15 | STA |
| Zry2-15 | 62/4/34 | 900 | 110/367/0.3 | ----- | ----- | ----- | SEM/EDS, AES |
| Zry2-15A | | | | steam | 700 | 2 | STA, SEM/EDS, AES |
| Zry2-15B | | | | | | 0.5 | STA, SEM/EDS, AFM, AES |
| Zry2-16 | 62/4/34 | 570 | 108/355/0.3 | ----- | ----- | ----- | XRD |
| Zry2-19A | Uncoated | ----- | ----- | steam | 700 | 10 | STA |
| Zry2-20A | 62/4/34 | 1100 | 62/4/34 | steam | 1100 | 0.5 | SEM |
| Zry2-21B | 62/4/34 | 1100 | 105/345/0.3 | BWR/ NWC | 288 | 48 | SEM, XRD |
| Zry2-23 | 62/4/34 | 1100 | 105/345/0.3 | ----- | ----- | ----- | AES, XRD |
| Zry2-23A | | | | steam | 700 | 6 | STA, AES, XRD |
| Zry2-23B | | | | | | 5 | STA, AES |
| Zry2-23C | | | | | | 2 | STA, AES |
| Zry2-23D | | | | | | 0.5 | STA, AES, XRD |
| Zry2-23E | | | | | | 10 | STA, AES, XRD |
| YSZ-1C | 62/4/34 | 570 | 108/355/0.3 | steam | 700 | 3.5 | SEM/EDS, AES |
| YSZ-2 | | | | ----- | ----- | ----- | XRD |
| YSZ-2A | | | | steam | 1100 | 2.5 | SEM/EDS, AES, XRD |
| YSZ-2B | | | | | 1250 | 1 | XRD |
| Si-1 | 62/4/34 | 1100 | 105/345/0.3 | ----- | ----- | ----- | SEM |

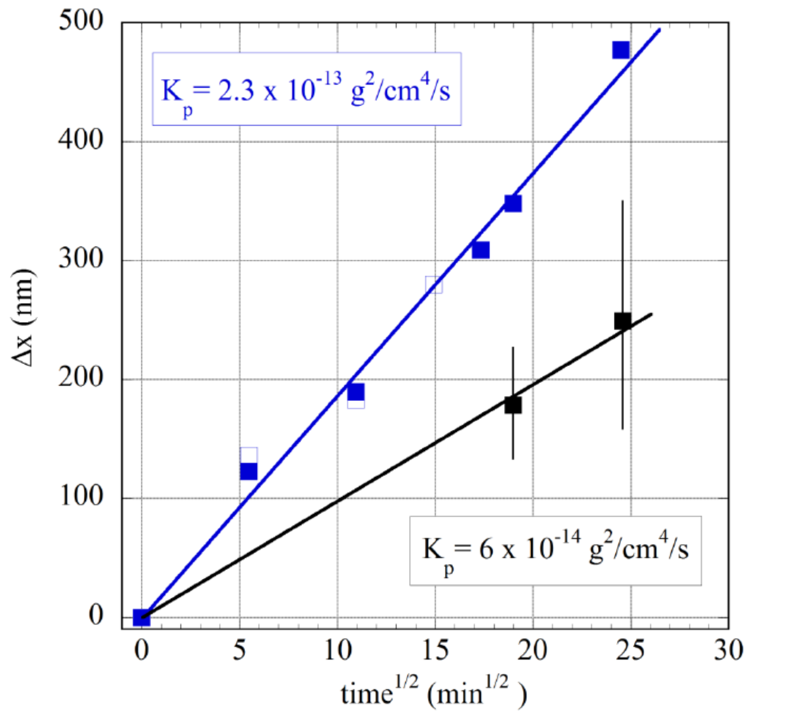
Δm vs. time
700 ºC steam



# AES elemental depth profiles 700 ºC steam

x = 1.1 µm
FeCrAl: 62-4-34

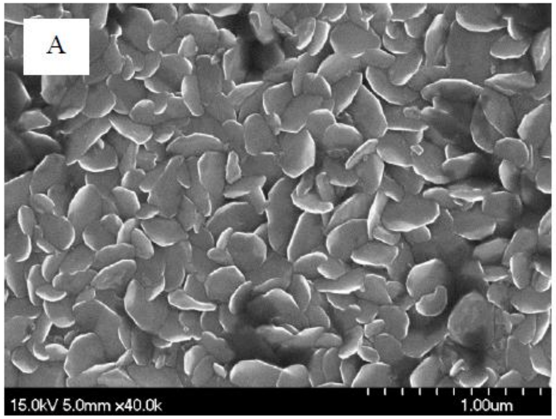


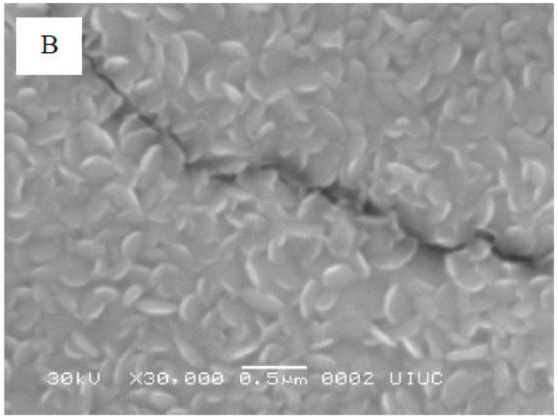



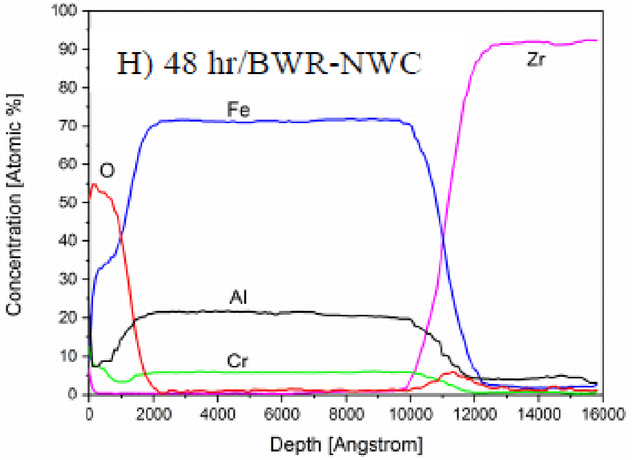

| Reference | $K_p = D_o exp(-E_a/kT)$ | | $K_p$ (700 ˚C) [$g^2/cm^4/s$] | 700 ˚C, 6 hour |
|---|---|---|---|---|
| | $D_o$ [$g^2/cm^4/s$] | $E_a$ [eV] | | Δx [nm] |
| [9] | 8.02 | 2.79 | 2.8 x $10^{-14}$ | 125 |
| [25] | 3.8x$10^{-8}$ | 1.46 | 1 x $10^{-15}$ | 25 |
| This work | AES | | 2.3(0.1) x $10^{-13}$ | 360 |
| | Profilometer | | 6(3) x $10^{-14}$ | 180 |

# Dynamic autoclave 288 ºC, BWR-NWC, 48 hours

x = 1.1 μm
FeCrAl: 62-4-34

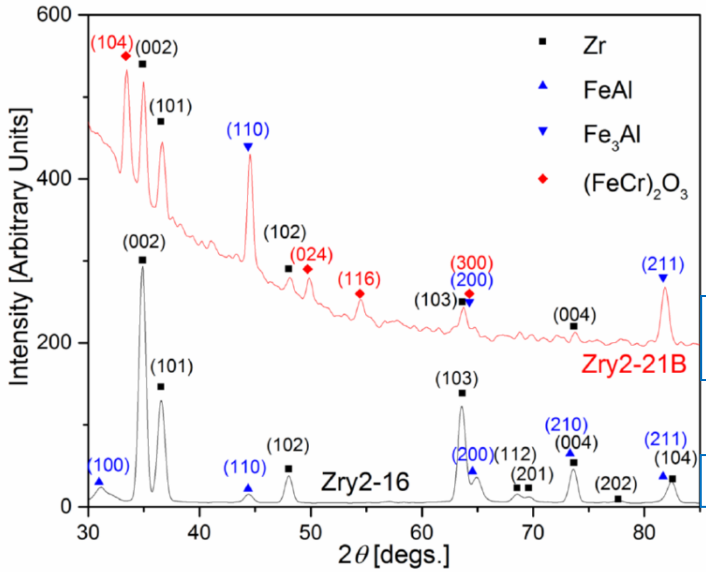



α-alumina like
$(FeCr)_2O_3$ (R-3c)

Glancing-angle XRD

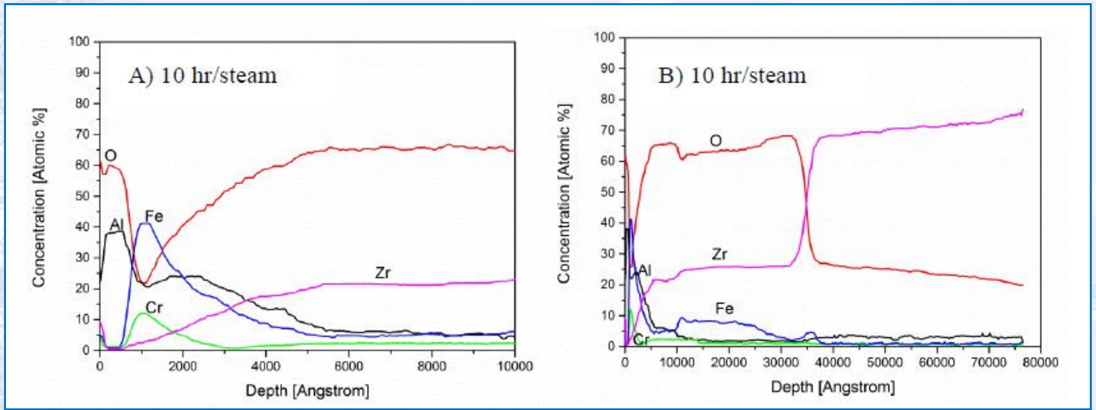



700 ºC
5 hr

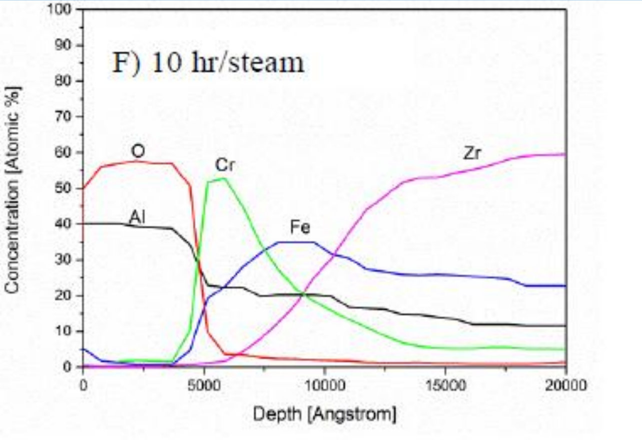
as-grown

# Effect of FeCrAl film thickness on zirconia growth in 700 ºC steam

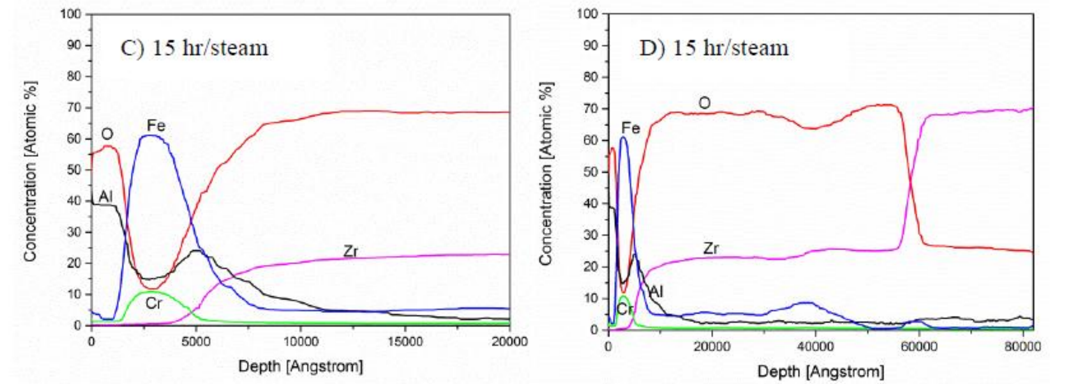
x = 0.3 μm



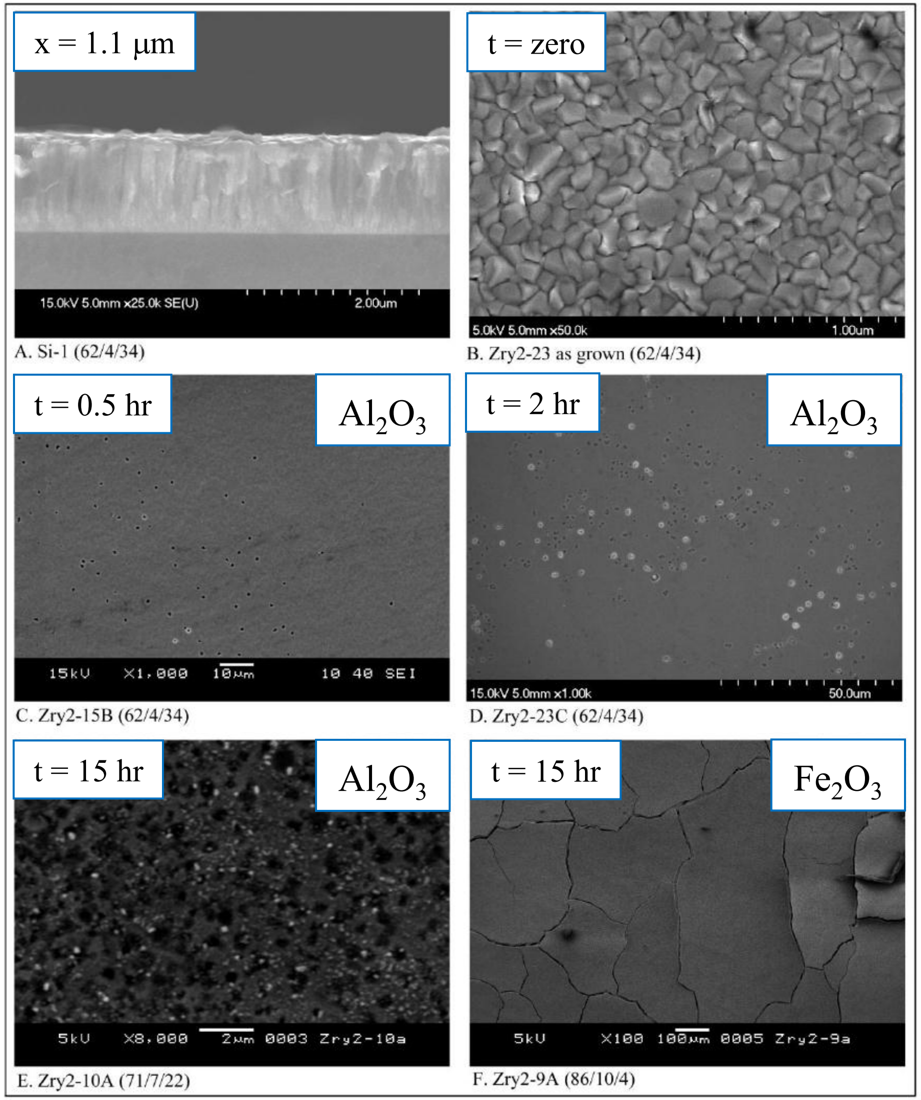

x = 1.1 μm



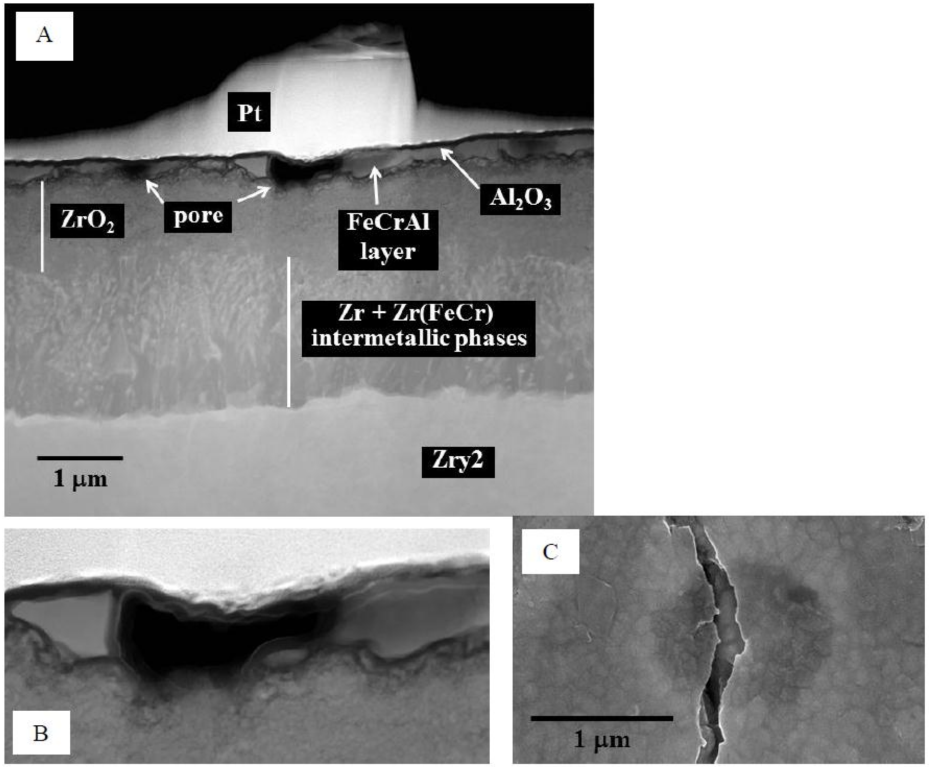

x = 0.6 μm



# Surface topography in 700 ºC steam vs. time, varying FeCrAl compositions




x = 0.3 µm

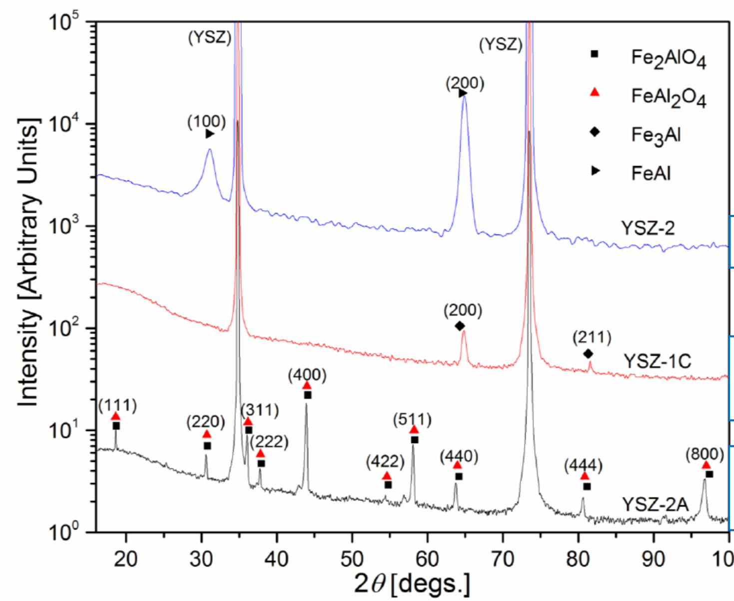


## Conclusions

- FeCrAl films perform satisfactorily in BWR-NWC environments.
- FeCrAl coatings with high Al compositions (>20 at. %) promote alumina formation during 700 ºC steam exposure.
- Alumina formation prevents zirconia formation of base Zircaloy.
- Fe-Zr 900 ºC eutectic will invalidate FeCrAl protection; buffer layer needed.
- The FeCrAl-YSZ system stable to steam at 1250 ºC; spinel formation.

# XRD analysis

## FeCrAl-YSZ



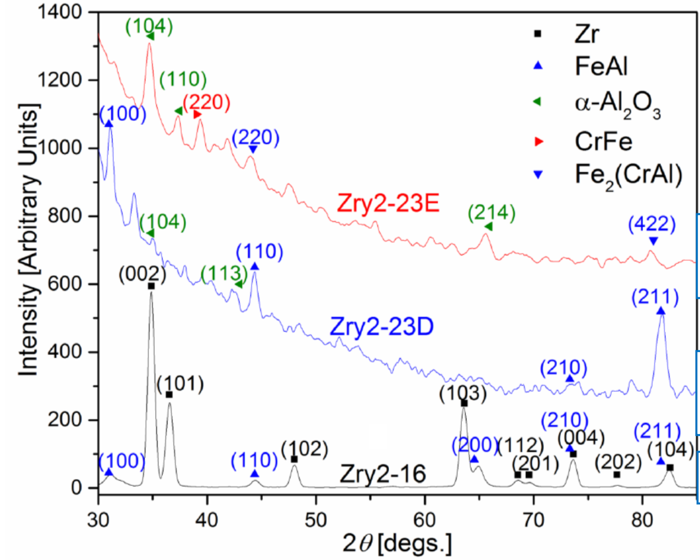

as-grown

700 ºC 3.5 hr

1100 ºC 2.5 hr

Figure 2. $\omega$-$2\theta$ specular XRD scans of Fe/Cr/Al:62/4/34 films on YSZ substrates: as-grown (YSZ-2), 700 °C steam exposure (YSZ-1C), and 1100 °C steam exposure (YSZ-2A). FeCrAl at this atomic composition grows as primitive cubic (Pm-3m), with (100) reflection intensity that otherwise is forbidden for the BCC structure. The as-grown FeCrAl film is highly textured since intensity from the (110) reflection, the strongest in the Pm-3m powder pattern, is absent.

## FeCrAl-Zircaloy 4




700 ºC 10 hr

700 ºC 0.5 hr

as-grown

Figure 3. $\omega$-$2\theta$ specular XRD scan of as-grown Fe/Cr/Al:62/4/34 on Zry2 (Zry2-16) and $2\theta$ glancing-angle scans of 0.5 hour (Zry2-23D) and 10 hour (Zry2-23E) 700-°C steam exposure. As with FeCrAl on YSZ, the FeCrAl film at this atomic composition grows as primitive cubic (Pm-3m). Unlike YSZ, however, the as-grown FeCrAl film is not textured and multiple reflections are observed from Zry2-16; all peaks can be indexed as Zr matrix or primitive cubic FeAl film reflections. Additional diffraction intensity indexed to α-alumina and a $Fe_2(CrAl)$ (Fd-3m) intermetallic phase is observed from the Zry2-23E sample exposed to 700 ºC steam for 10 hours. The unindexed Zry2-23D and Zry2-23E diffraction intensity (for example, at $2\theta$~32º in the Zry2-23D pattern, at $2\theta$~41-43 º and 47º in Zry2-23E) is likely due to intermetallic phase formation involving a combination of Fe, Al, Cr, and Zr.