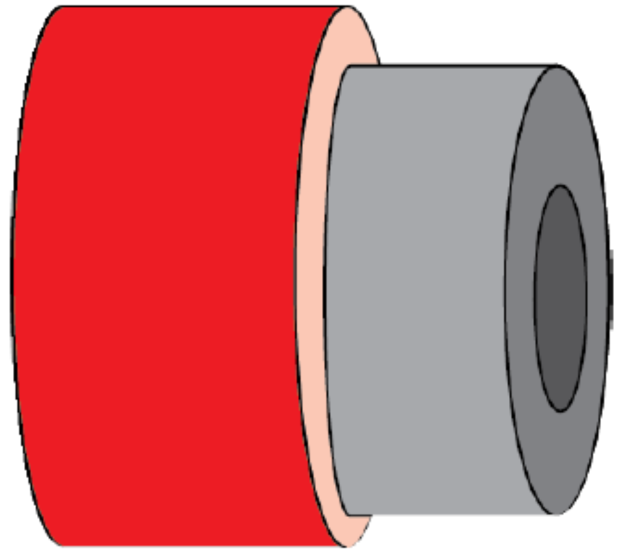

# Ceramic Coatings for Clad (The $C^3$ Project)

Advanced Accident-Tolerant Ceramic Coatings for Zr-Alloy Cladding


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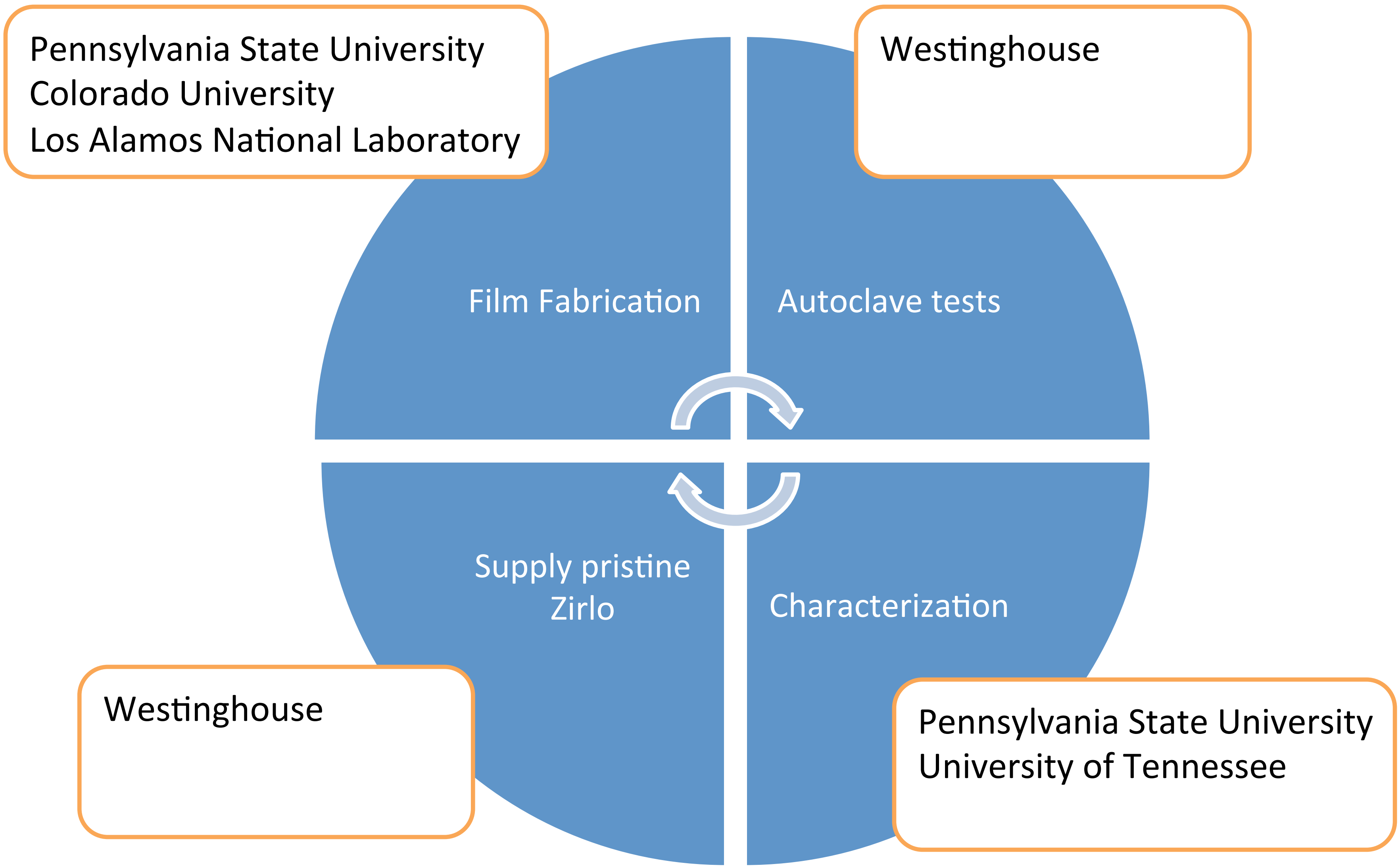
*University of Tennessee, Knoxville*

# Project Objective:

The goal of this NEUP-IRP project is to develop a fuel concept based on an advanced ceramic coating for Zr-alloy cladding. The coated cladding must exhibit demonstrably improved performance compared to conventional Zr-alloy clad in the following respects:

1. During normal service, the ceramic coating should decrease cladding oxidation and hydrogen pickup (the latter leads to hydriding and embrittlement).

2. During a reactor transient (e.g., a loss of coolant accident), the ceramic coating must minimize or at least significantly delay oxidation of the Zr-alloy cladding, thus reducing the amount of hydrogen generated and the oxygen ingress into the cladding.


Pennsylvania State University
Colorado University
Los Alamos National Laboratory
Westinghouse
Film Fabrication
Autoclave tests
Supply pristine Zirlo
Characterization
Westinghouse
Pennsylvania State University
University of Tennessee

# Fabrication Techniques

## Pennsylvania State University
### Cathodic arc physical vapor deposition

- A voltage is applied to the cathode while a grounded trigger contacts the cathode to initiate the arc.
- Arc movement is constrained to the target face using magnets.
- cathode spots vary in size from about 1-10 microns, have a high current density ($10^6$-$10^8$ A-cm$^{-2}$), and their lifetime is about 10 nanoseconds to 1 microsecond.
- Accumulation of these cathode spots creates a dense plasma of the cathode material.
- The high pressure of the cathode spot ejects ionized and molten material from the cathode surface into the chamber, thus forming the plasma.
- Plasma generation is proportional to the supplied current by the power supply.
- Plasma is ionized with energetic ions to promote the adhesion and formation of dense coatings on the substrate.

## University of Colorado
### Pulsed Liquid Injection

- Coatings will be made from liquid organic precursors with "silazane based" chemistries.
- Lead to amorphous ceramics constituted from Si-C-N-O.
- These materials develop graphene networks within them, which serve as diffusion barriers to atmospheric species.
- Coatings are being deposited primarily in a pulsed liquid injection reactor.
- "cold wall" reactor the precursor is nebulized through an ultrasonic nozzle and the polymer layer deposited on the substrate in this way is cured, in-situ, with a radiation furnace.
- The process is cycled to build up the thickness of the coating from a fraction of a micrometer up to a few micrometers.

## Los Alamos National Laboratory
### Electrospark deposition

- Electrospark deposition (ESD) is a pulsed micro-welding process.
- ESD equipment contains a capacitor-based power supply that produce short duration, high current pulses through a rotating rod consumable electrode.
- The consumable electrode material is deposited onto the work piece by means of electric sparks.
- The electrode is the anode and the substrate is the cathode.
- When the capacitor energy is released, the direct current generates a plasma arc at a high temperature (8000 to 25,000°C) between the tip of the electrode and the substrate.
- The plasma arc ionizes the consumable and a small quantity of molten electrode material is transferred onto the substrate.
- The transfer of material is rapid and the self-quenching is extremely fast.

# Penn. State Deposition process (Gen 1)

***Sample preparation:***

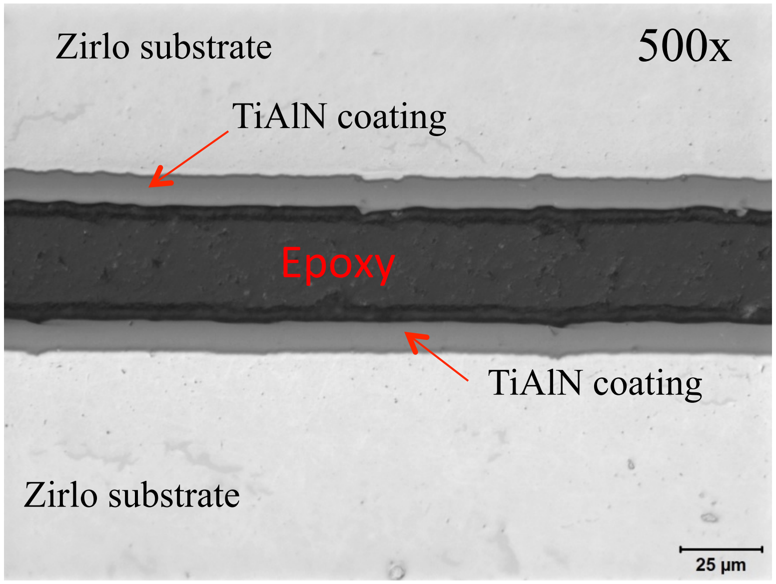
- Flat plate Zirlo samples were sheared to approximately 1” x 2” using a bench shear.
- Tubes of Zirlo 2” long and 3/8” dia.
- Flat plate surfaces and edges were hand ground with 240 SiC grit.
- Process repeated with 600 SiC grit and 800 SiC grit paper to obtain a surface roughness (~10 μin Ra).
- Samples were marked with identification using a diamond scribe on one of the sides (PF##, P for Penn state, F for flat).
- Hole drilled through the samples for mounting in the autoclave system.
- Samples were ultrasonically cleaned in acetone for 20 minutes and N2 dried, followed by 20 minute ultrasonic clean in methanol and N2 drying.

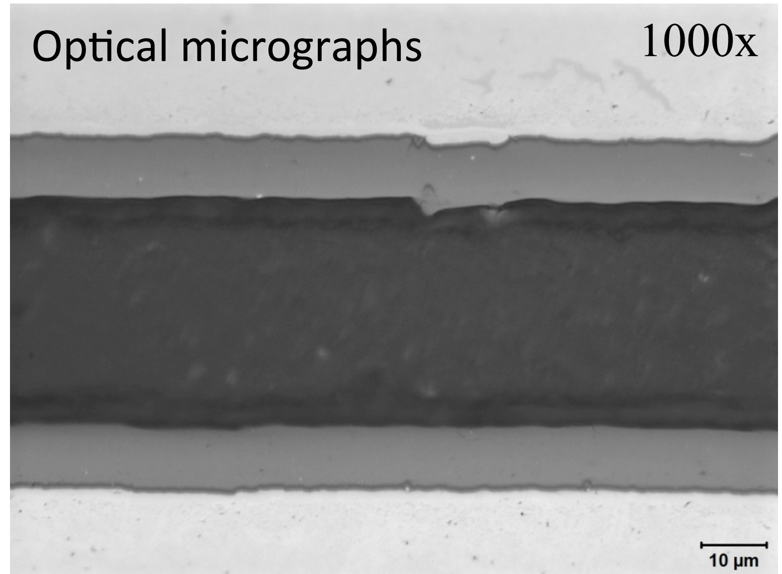

***Cathodic arc deposition of TiAlN (10-12 microns):***

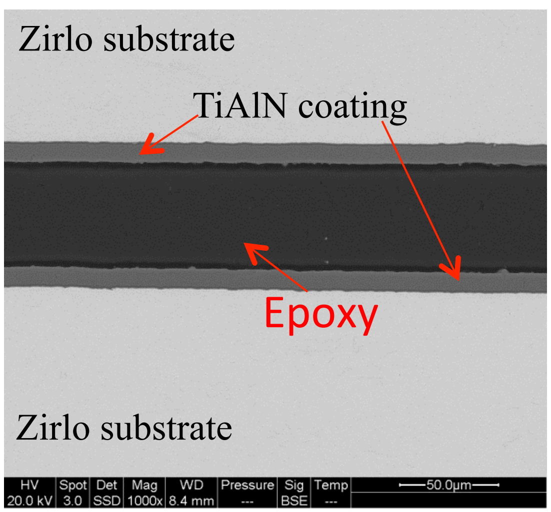
- TiAl alloy target with a ratio of 33 at% Ti to 67 at% Al (50-50 wt.%).
- Substrate temperature was 250°C.
- Deposition rate of 0.028 microns/min (1.68 microns/hour).
- Chamber base pressure of 2 x $10^{-6}$ mTorr.
- The samples were then ion etched in a 1.2 x $10^{-2}$ mTorr argon atmosphere at a -1000V bias.
- A metallic *Ti bond layer (200-1000 nm)* was deposited.
  Nitrogen gas was introduced into the chamber in order to react with the TiAl metallic vapor to form the TiAlN coatings.
- ***Primary deposition parameters used for monolithic TiAlN coatings (15 μm):*** 12 mTorr $N_2$ pressure, -50V substrate bias, and 65 A and 60 A evaporator current for Ti and TiAl cathodes, respectively.

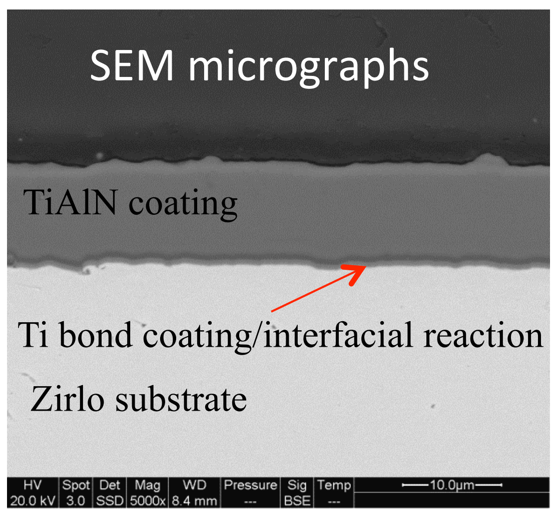
# Penn. State coatings: as deposited

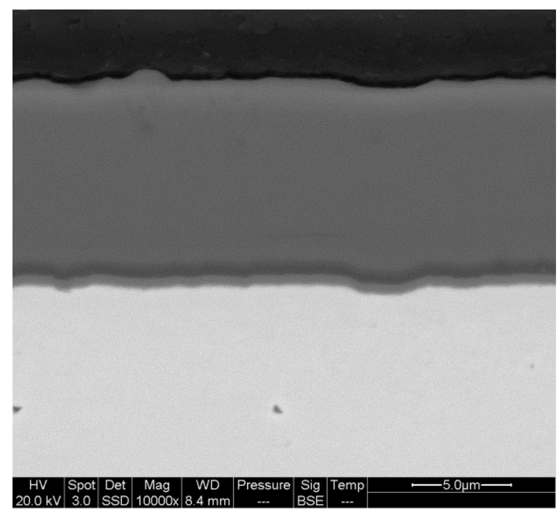
TiAlN (9.24 μm)/Ti BC (600 nm)/ Zirlo



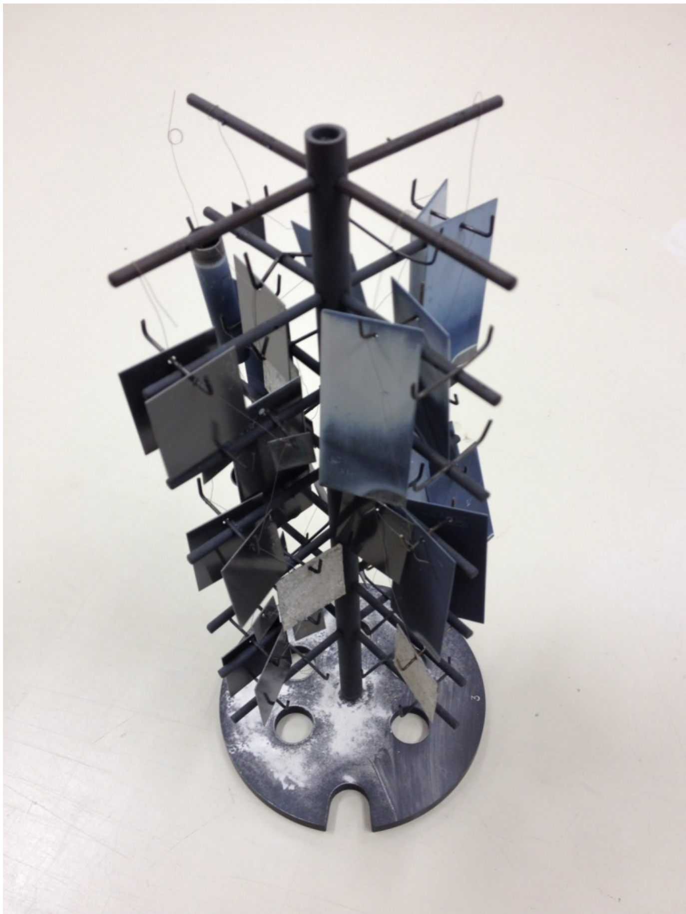



# Sample list for Gen. 1 samples from Penn. State

| | Sample ID | ARL/PSU ID | Description |
|---|---|---|---|
| 1 | PF13 | C131513-1H | TiAlN (~13mm) / Ti BC (200nm) coated zirlo |
| 2 | PF18 | C130515-1H | TiAlN (~13mm) / Ti BC (400nm) coated zirlo |
| 3 | PF31 | C130529-1F | TiAlN (TBD) / Ti BC (600nm) coated zirlo |
| 4 | PF35 | C130531-1E | TiAlN (TBD) / Ti BC (600nm) coated zirlo - NoRB |
| 5 | PF36 | C130531-1F | TiAlN (TBD) / Ti BC (600nm) coated zirlo |
| 6 | PF4 | C130508-1D | TiAlN (~13mm) / Ti BC (600nm) coated zirlo |
| 7 | PF21 | C130517-1F | TiAlN (~12mm) / Ti BC (600nm) coated zirlo (uncoated fixturing area sectioned) |
| 8 | PF22 | C130517-1G | TiAlN (~12mm) / Ti BC (600nm) coated zirlo |
| 9 | PF28 | C130521-1H | TiAlN (~14mm) / Ti BC (800nm) coated zirlo |
| 10 | PT1 | C131513-1A | TiAlN (~13mm) / Ti BC (200nm) coated zirlo |
| 11 | PT5 | C130515-1B | TiAlN (~13mm) / Ti BC (400nm) coated zirlo |
| 12 | PT16 | C130531-1A | TiAlN (TBD) / Ti BC (600nm) coated zirlo |
| 13 | PT9 | C130517-1C | TiAlN (~12mm) / Ti BC (600nm) coated zirlo |
| 14 | PT11 | C130521-1B | TiAlN (~14mm) / Ti BC (800nm) coated zirlo |

***Primary test variable was titanium bond coating thickness***

# Westinghouse autoclave tests

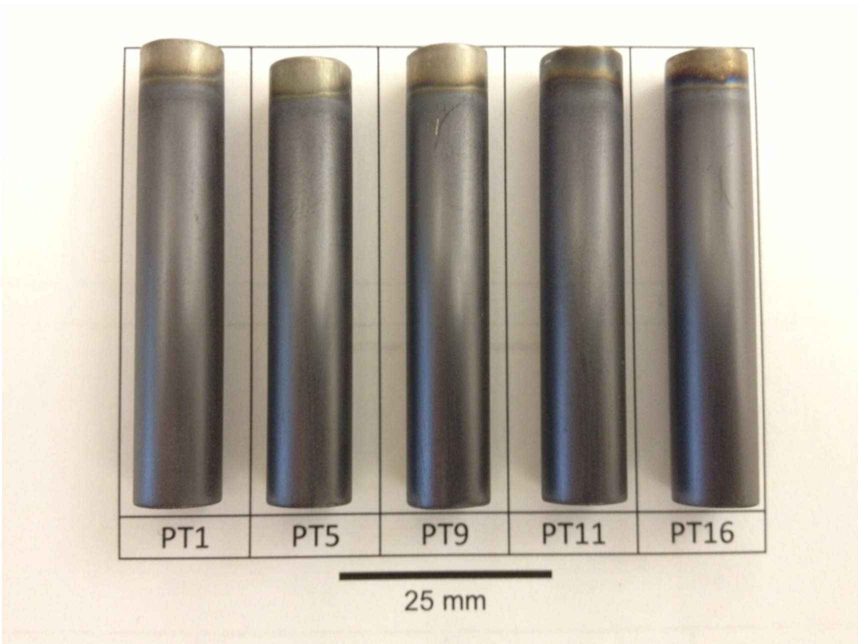


***Autoclave test parameters (ASTM: G2/G2M)***

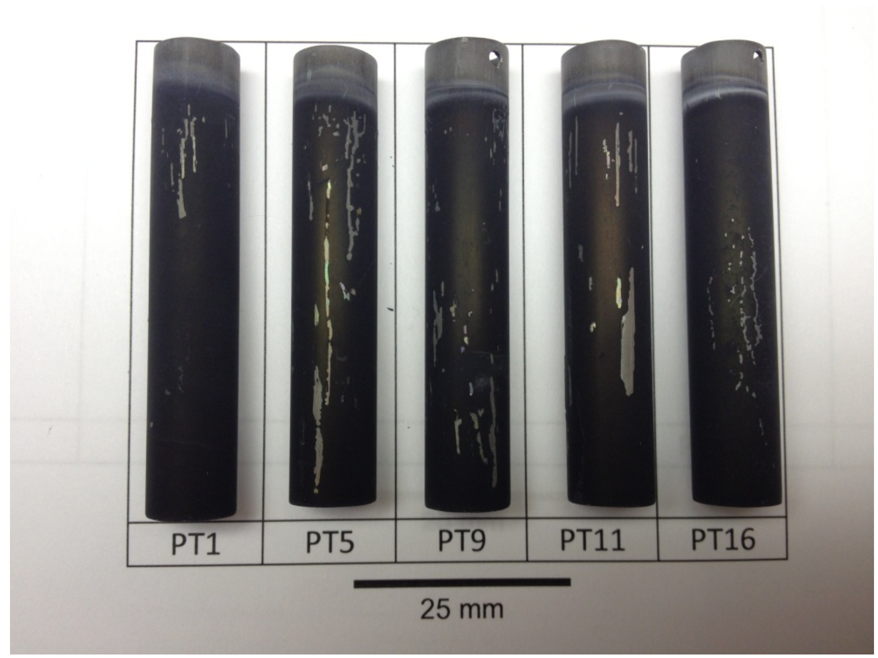
- Samples cleaned by ultrasonicating and dried.
- Samples submerged in ½ gallon of static water.
- Temperature raised to 360 $^{o}$C for 3 days.
- Samples removed and weighed

# Penn. State autoclave results (360 $^{o}C$ Water 3 days) (Gen 1)
## ***<u>Tubes</u>***

Pre-test

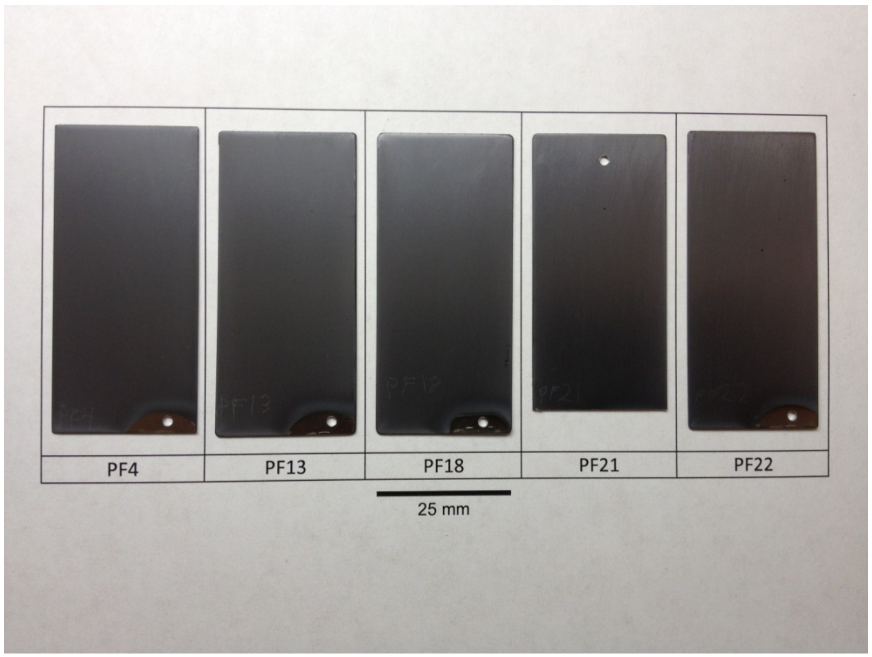



Post-test

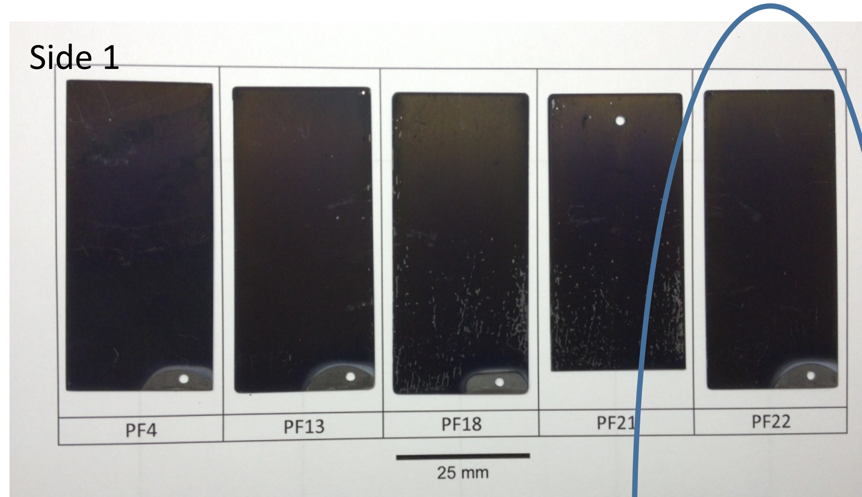


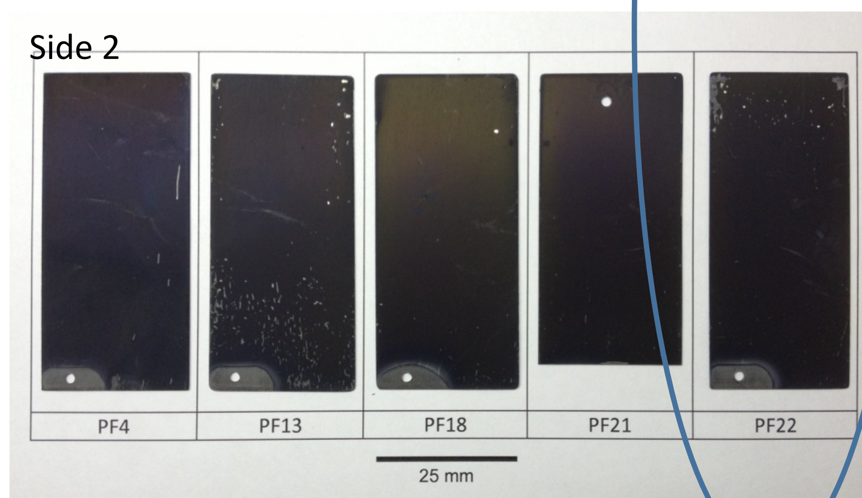
# Penn. State autoclave results (360 $^{o}$C Water 3 days) (Gen 1)
## ***Flat plates***

Pre-test



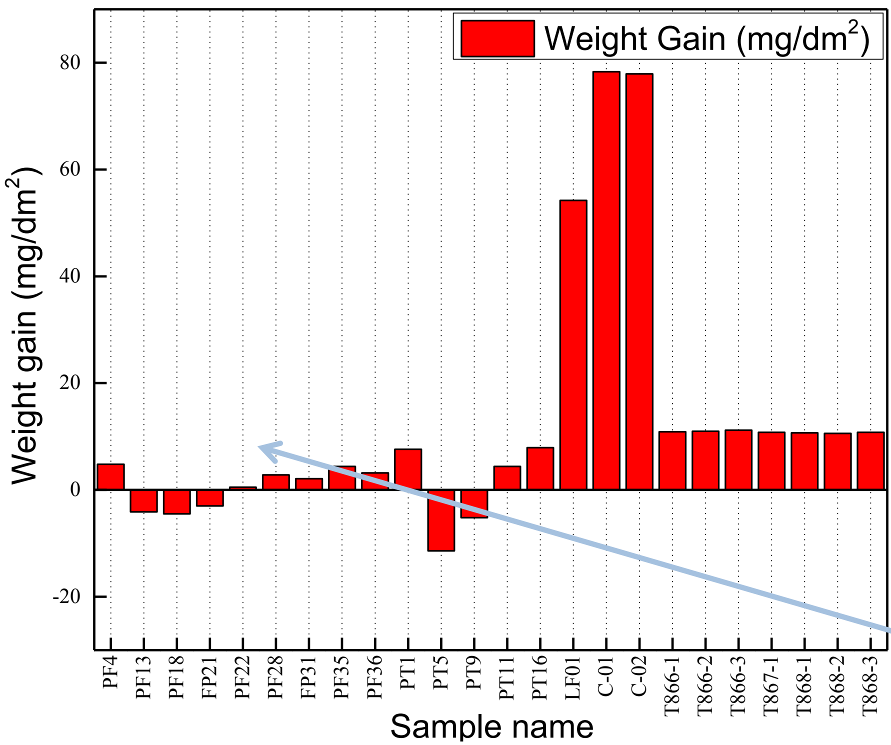

Post-test

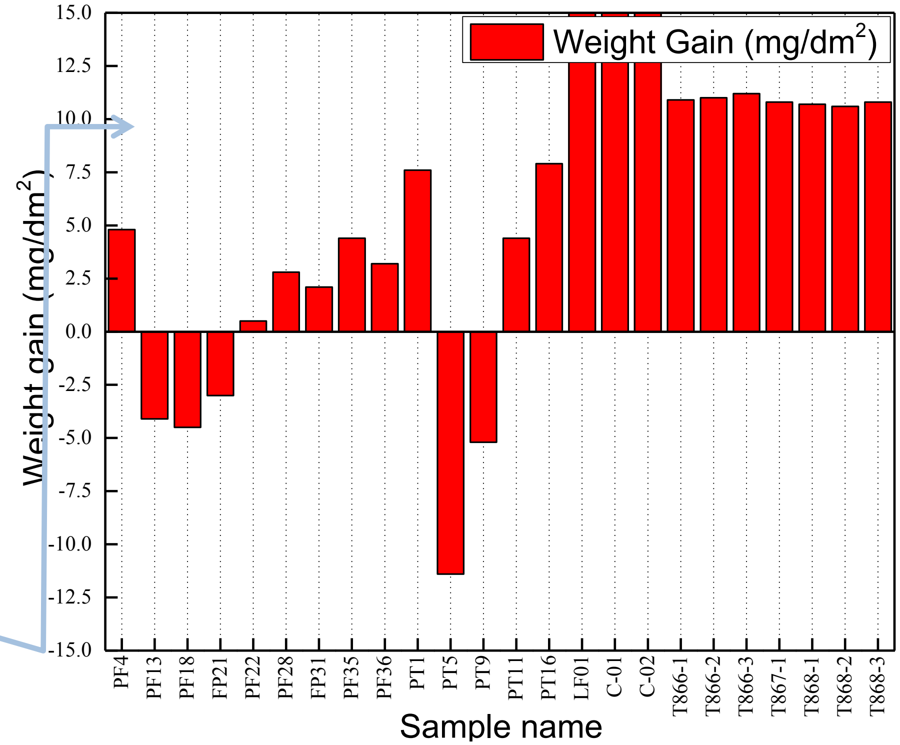


# Autoclave results (360 °C Water 3 days) (Gen 1)

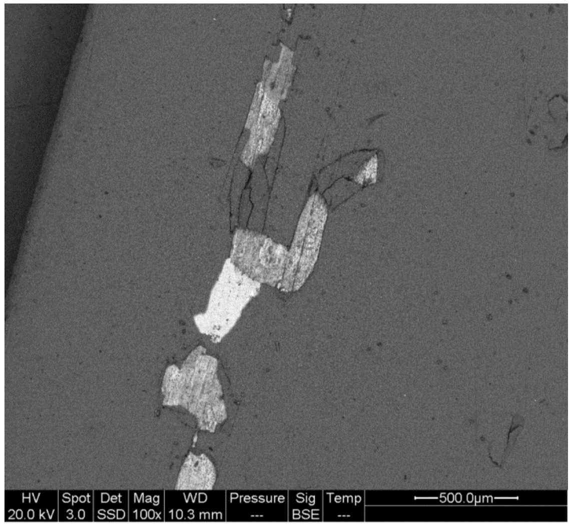
## *Weight gain*

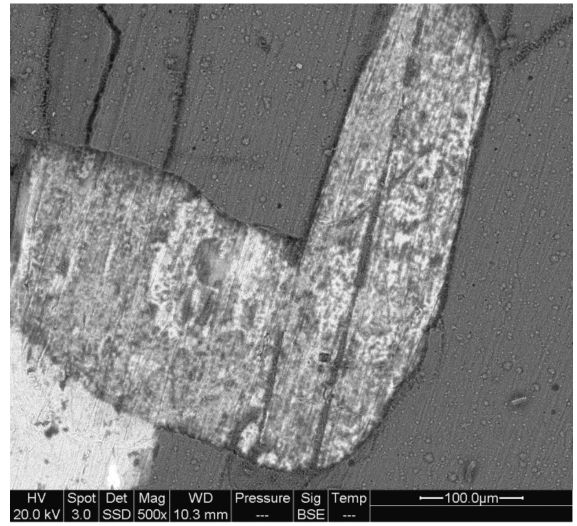


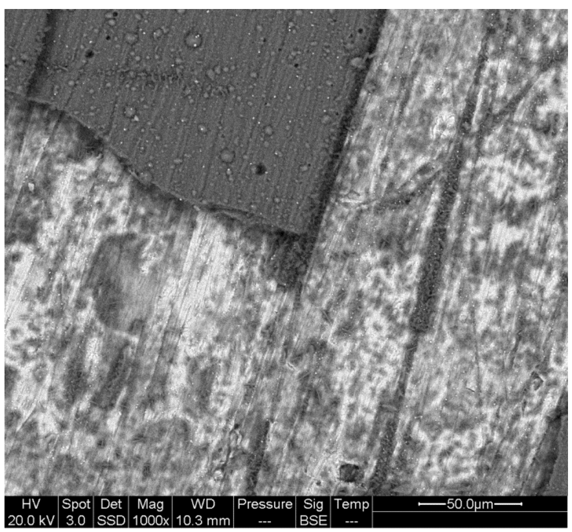



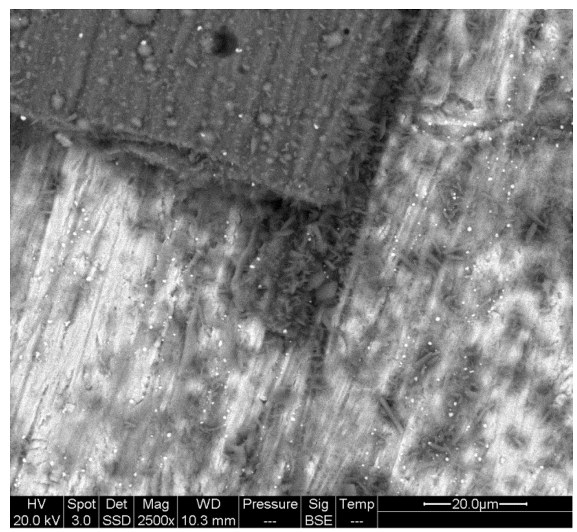
# Penn. State autoclave results (360 $^{o}$C Water 3 days) (Gen 1) ***SEM***

(PF21): TiAlN (11.96 µm)/Ti BC (600 nm)/ Zirlo



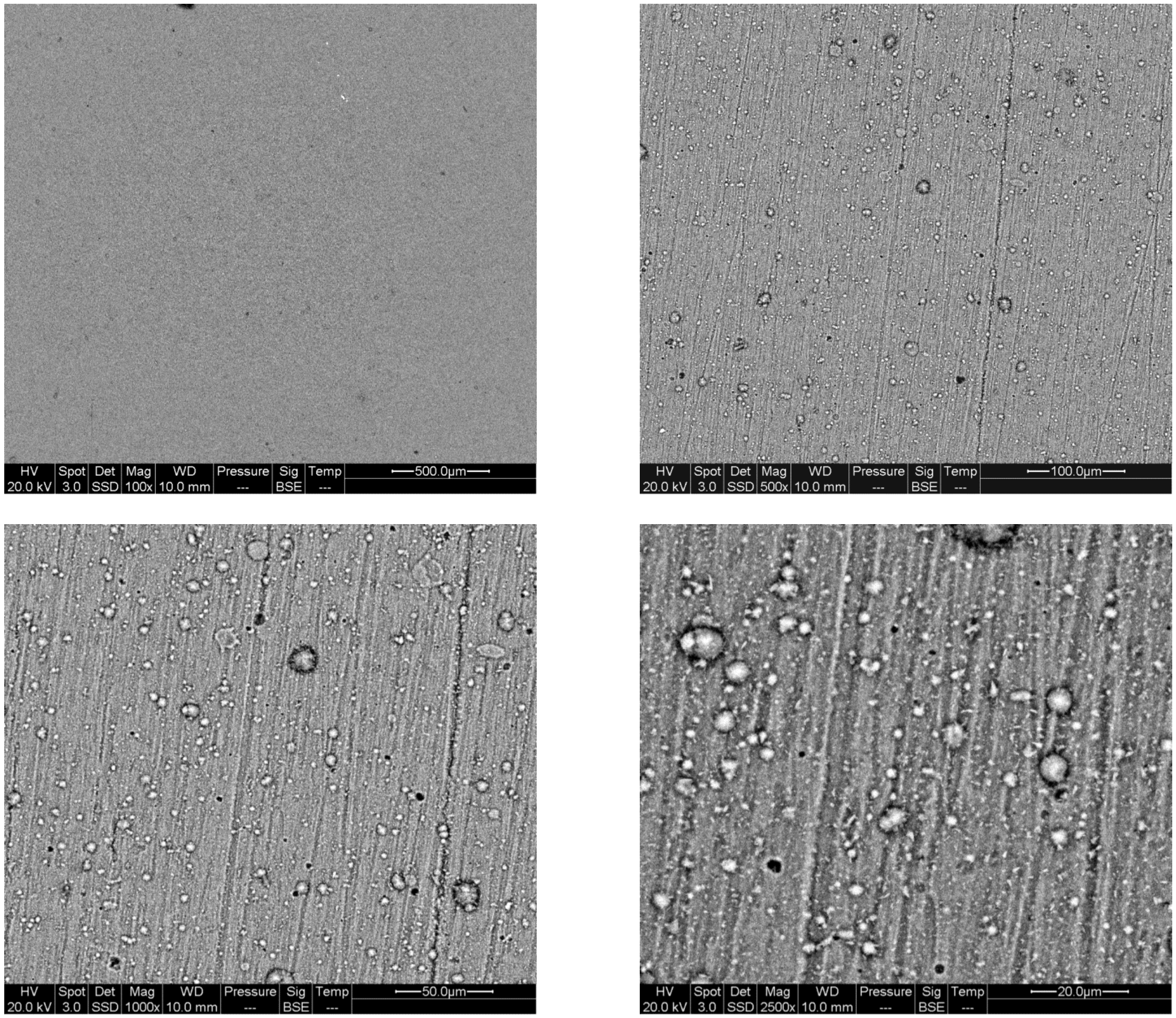



# Penn. State autoclave results (360 $^{o}$C Water 3 days) (Gen 1)
## ***SEM***

(PF35):TiAlN (9.24 µm)/Ti BC (600 nm)/ Zirlo

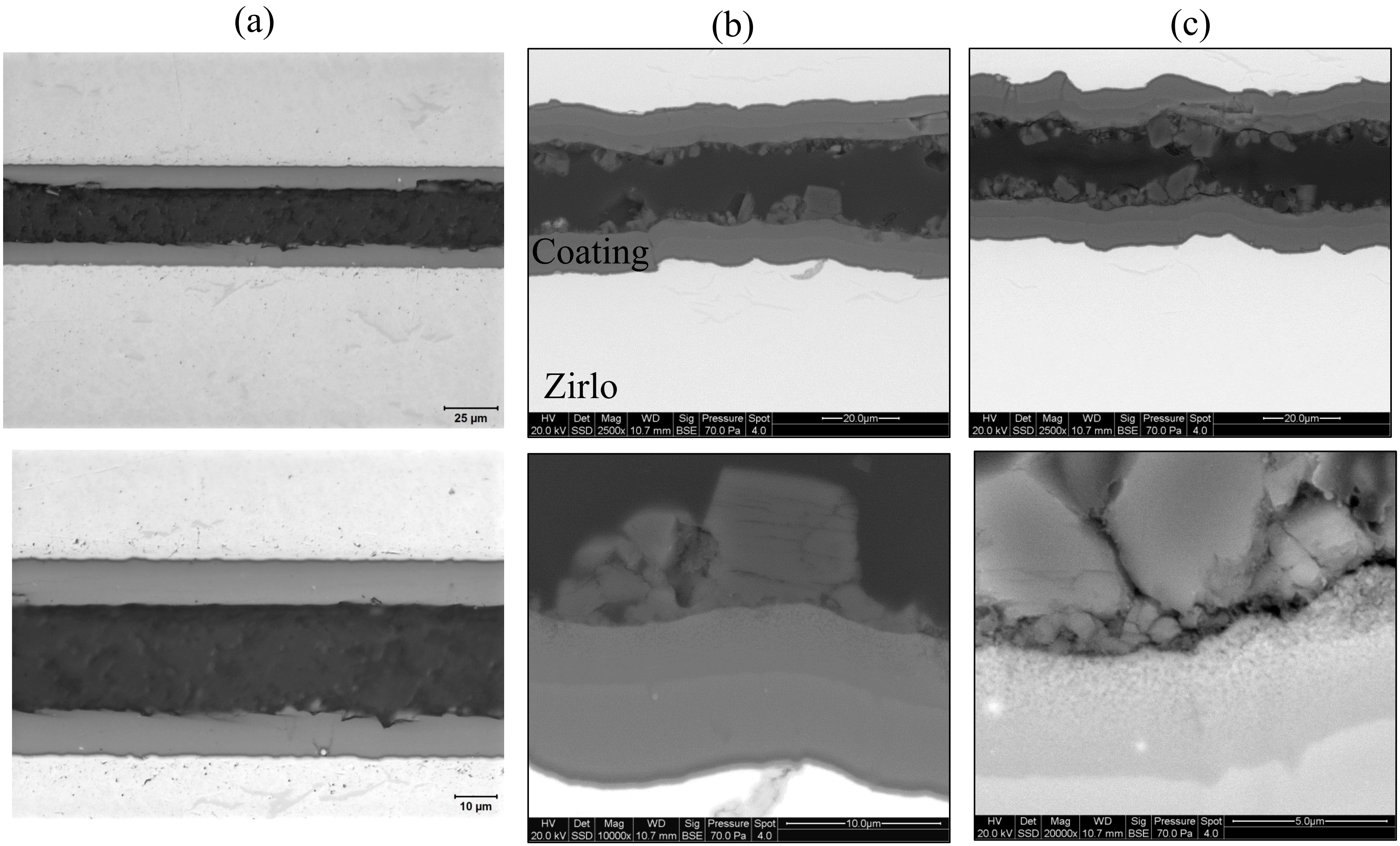


# Sample list for Gen. 2 samples from Penn. State

| | Sample ID | ARL/PSU ID | Description |
|---|---|---|---|
| 1 | PF59 | C130620-1H | TiAlN (~12µm) / Ti BC (600nm) (35µin Ra) coated zirlo |
| 2 | PF61 | C130625-1C | TiAlN (~12µm) / Ti BC (600nm) (20µin Ra) coated zirlo |
| 3 | PF65 | C130625-1G | TiAlN (~12µm) / Ti BC (600nm) (4µin Ra) coated zirlo |
| | | | |
| 4 | PF41 | C130614-1E | TiAlN (~8µm) / Ti BC (600nm) (35µin Ra) coated zirlo |
| 5 | PF43 | C130614-1G | TiAlN (~8µm) / Ti BC (600nm) (20µin Ra) coated zirlo |
| 6 | PF46 | C130618-1F | TiAlN (~8µm) / Ti BC (600nm) (4µin Ra) coated zirlo |
| | | | |
| 7 | PF49 | C130620-1A | TiAlN (~4µm) / Ti BC (600nm) (35µin Ra) coated zirlo |
| 8 | PF51 | C130620-1C | TiAlN (~4µm) / Ti BC (600nm) (20µin Ra) coated zirlo |
| 9 | PF53 | C130620-1E | TiAlN (~4µm) / Ti BC (600nm) (10µin Ra) coated zirlo |
| 10 | PF55 | C130620-1G | TiAlN (~4µm) / Ti BC (600nm) (4µin Ra) coated zirlo |
| | | | |
| 11 | PF69 | C130627-1C | TiAlN (~4µm) / Ti BC (600nm) (10µin Ra) coated zirlo (two sided coating) |
| 12 | PF71 | C130627-1E | TiAlN (~4µm) / Ti BC (600nm) (10µin Ra) coated zirlo only one side coated |
| 13 | PF73 | C130627-1G | TiAlN (~4µm) / Ti BC (600nm) (4µin Ra) coated zirlo (two sided coating) |
| 14 | PF75 | C130627-1I | TiAlN (~4µm) / Ti BC (600nm) (4µin Ra) coated zirlo only one side coated |
| | | | |
| 15 | PT19 | C130614-1A | TiAlN (~8mm) / Ti BC (600nm) (35µin Ra) coated zirlo |
| 16 | PT22 | C130618-1B | TiAlN (~8mm) / Ti BC (600nm) (20µin Ra) coated zirlo |
| 17 | PT23 | C130618-1C | TiAlN (~8mm) / Ti BC (600nm) (4µin RA) coated zirlo |

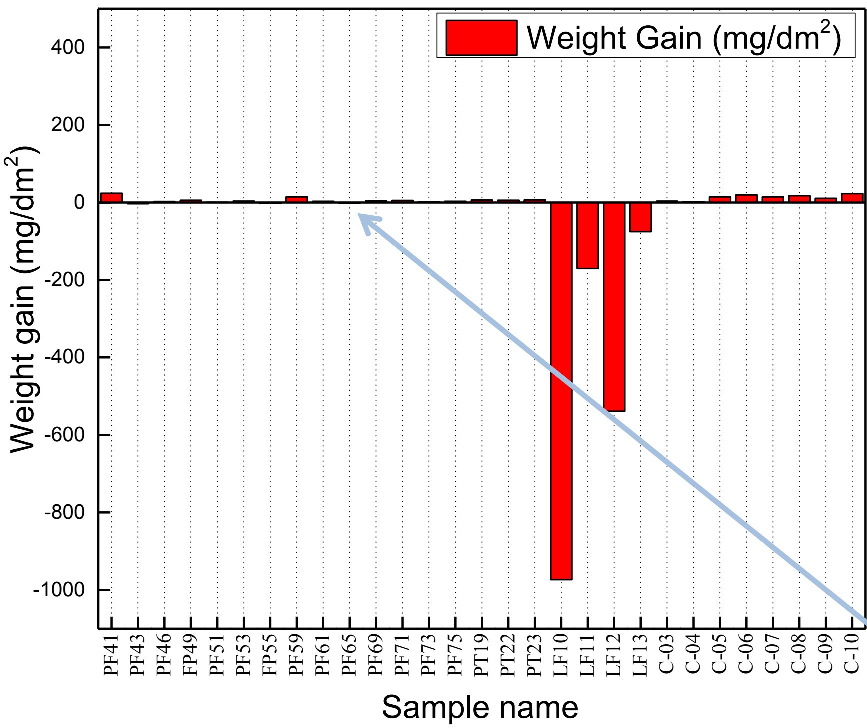
***Primary test variable was TiAlN coating thickness and substrate surface roughness***

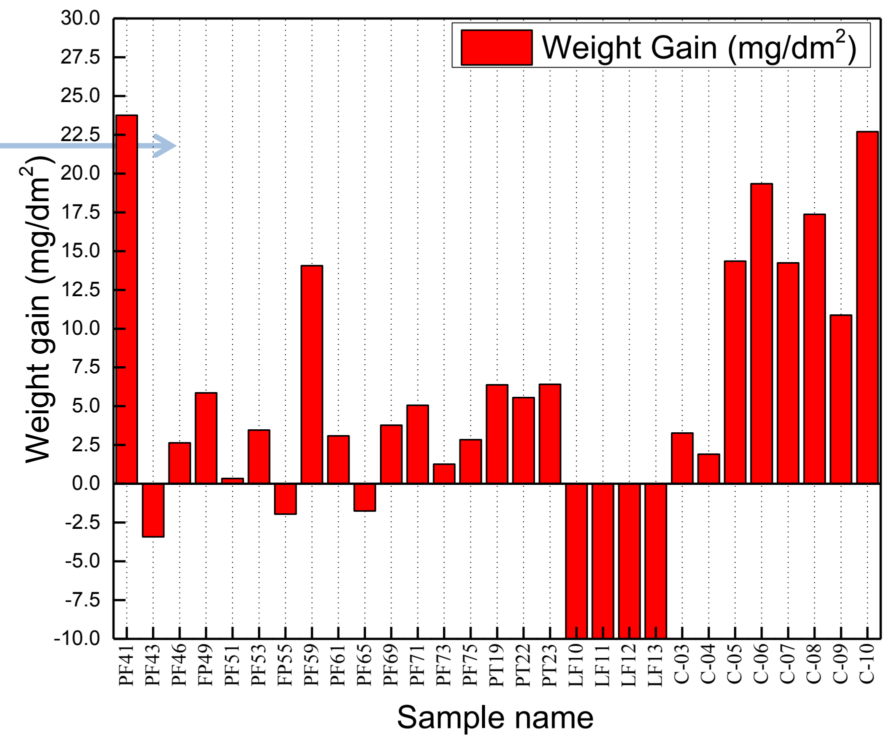
# C130625-1A (PF59):
# TiAlN (~12 µm)/Ti BC (600 nm)/ Zirlo (35 µin Ra)



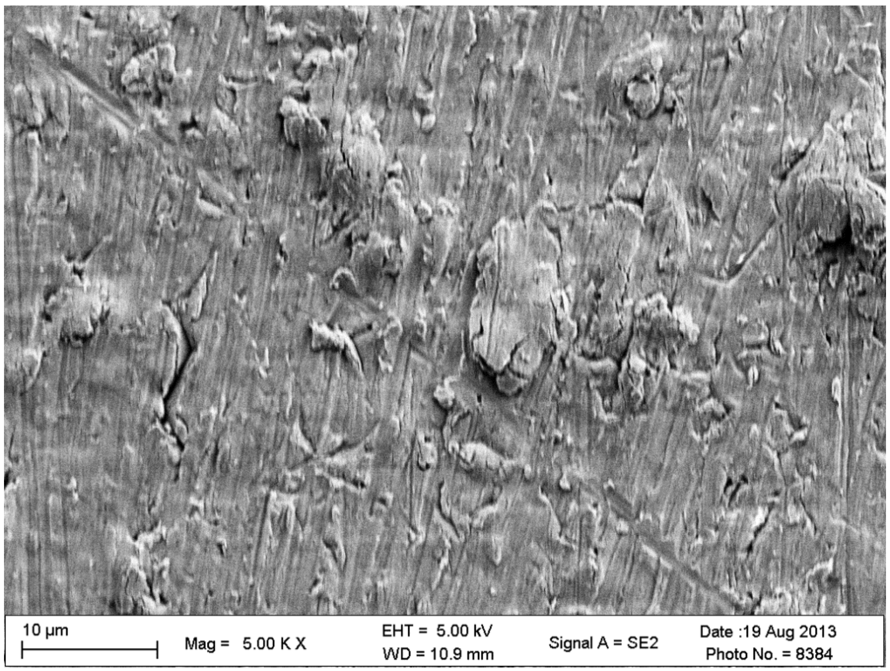

TiAlN deposited onto a zirlo substrate (a) Optical image of polished cross section in "as deposited" condition, (b) ESEM image after autoclave, and (c) ESEM image after autoclave testing.

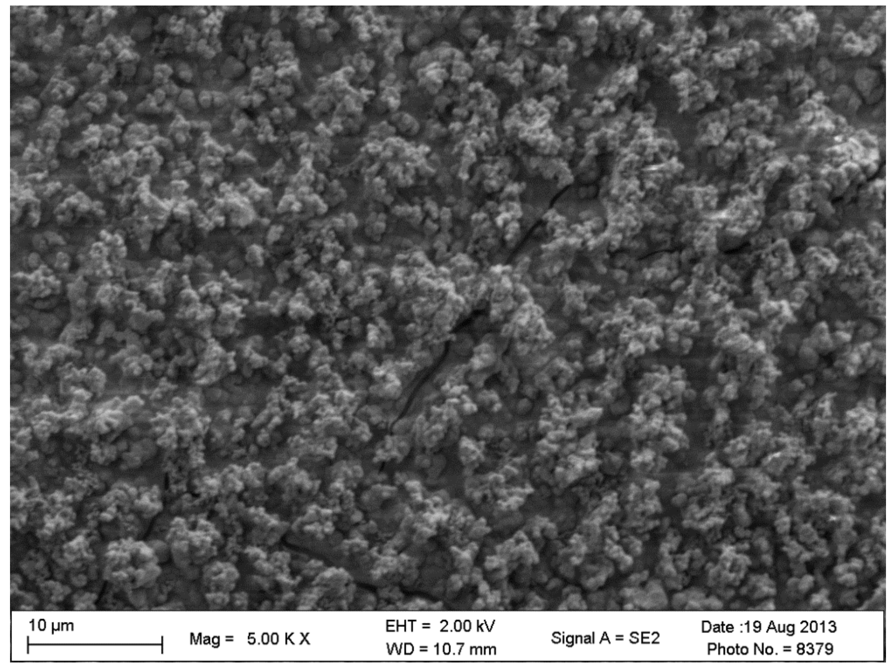
# Autoclave results (360 ºC Water 3 days) (Gen 2)
## *Weight gain*



# Univ. Colorado autoclave results (360 $^{o}$C Water 3 days) (Gen 2) ***SEM***



# Modeling efforts at Penn. State

- Considered fuel performance based on possible coating on cladding.
  - Determined Effective Full Power Days (EPFD) penalty.
  - Fuel enrichment percentage to match a reference cycle length
  - Increase of centerline temperature
- Results indicate that thickness more than composition responsible for penalties.

Cycle Length Penalty (EPFD) derived from coatings
as a function of their composition and thickness

| Coating | 10 µm | 50 µm | 100 µm |
|---|---|---|---|
| $Ti_3AlC_2$ | -3.7 | -19.0 | -39.8 |
| $Ti_2AlC$ | -3.7 | -17.4 | -35.0 |
| $Nb_2AlC$ | -2.8 | -14.5 | -28.0 |
| TiAlN | -3.4 | -16.9 | -35.3 |

Fuel Enrichment (%) that matches the reference cycle length as a function of composition and thickness. Reference fuel 4.5% enrichment.

| Coating | 10 µm | 50 µm | 100 µm |
|---|---|---|---|
| $Ti_3AlC_2$ | 4.53 | 4.70 | 4.9 |
| $Ti_2AlC$ | 4.53 | 4.68 | 4.84 |
| $Nb_2AlC$ | 4.52 | 4.64 | 4.8 |
| TiAlN | 4.53 | 4.68 | 4.86 |

Centerline Fuel Temperature increase ($^{o}$C) in steady-state conditions as a function of coatings composition and thickness

| Coating | 10 µm | 50 µm | 100 µm |
|---|---|---|---|
| $Ti_3AlC_2$ | 0.1 | 0.7 | 1.5 |
| $Ti_2AlC$ | 0.2 | 0.9 | 1.8 |
| $Nb_2AlC$ | 0.2 | 1.1 | 2.1 |
| TiAlN | 1.3 | 6.4 | 12.8 |

# Future Plans

- Penn. State Univ.:
  - Surface preparation of Zirlo
  - MAX phase coatings
- University of Colorado:
  - Further characterization the bond coat
  - Greater adhesion of the Si-C-N-O bond coat
- Los Alamos Natl. Lab. (LANL):
  - Thermal spray MAX phase coatings on Zirlo
- Univ. of Tennessee:
  - Magnetron sputtering of combinatorial MAX phase films
  - GXRD and XSEM of as deposited and autoclaved samples from Univ. Colorado and LANL
  - Explore ion-beam techniques to modify the surface of Zirlo (With Univ. Michigan)
- UK:
  - Fabrication of sputtering targets of MAX phase compounds
  - Hot Iso-static Pressing (HIP) of coatings

***More advanced characterization efforts***

# Thanks

| Thickness, μm | Coating | Burnup difference, GWd/t | Cycle length difference, EFPD |
|---|---|---|---|
| 10 | $Ti_3AlC_2$ | -0.5 | -4.2 |
| | $Ti_2AlC$ | -0.4 | -3.4 |
| | $Nb_2AlC$ | -0.4 | -3.6 |
| | TiAlN | -0.4 | -3.6 |
| | ZrC | -0.1 | -0.9 |
| 50 | $Ti_3AlC_2$ | -2.3 | -20.1 |
| | $Ti_2AlC$ | -2.0 | -17.9 |
| | $Nb_2AlC$ | -1.9 | -16.7 |
| | TiAlN | -2.1 | -18.7 |
| | ZrC | -0.8 | -7.0 |
| 100 | $Ti_3AlC_2$ | -4.6 | -40.5 |
| | $Ti_2AlC$ | -4.2 | -37.1 |
| | $Nb_2AlC$ | -3.9 | -34.3 |
| | TiAlN | -4.2 | -36.9 |
| | ZrC | -1.4 | -12.3 |

| Thickness, μm | Coating | $T_{cl}$, K | $\Delta T_{cl}$, K |
|---|---|---|---|
| No Coating | | 1354.8 | 0 |
| 10 | $Ti_3AlC_2$ | 1354.9 | +0.1 |
| | $Ti_2AlC$ | 1355.0 | +0.2 |
| | $Nb_2AlC$ | 1355.0 | +0.2 |
| | TiAlN | 1356.1 | +1.3 |
| | ZrC | 1355.1 | +0.3 |
| 50 | $Ti_3AlC_2$ | 1355.5 | +0.7 |
| | $Ti_2AlC$ | 1355.7 | +0.9 |
| | $Nb_2AlC$ | 1355.9 | +1.1 |
| | TiAlN | 1361.2 | +6.4 |
| | ZrC | 1356.4 | +1.6 |
| 100 | $Ti_3AlC_2$ | 1356.2 | +1.4 |
| | $Ti_2AlC$ | 1356.6 | +1.8 |
| | $Nb_2AlC$ | 1356.9 | +2.1 |
| | TiAlN | 1367.6 | +12.8 |
| | ZrC | 1358.0 | +3.2 |