Advanced Composite Coatings for Industries of the Future (Project 1791)

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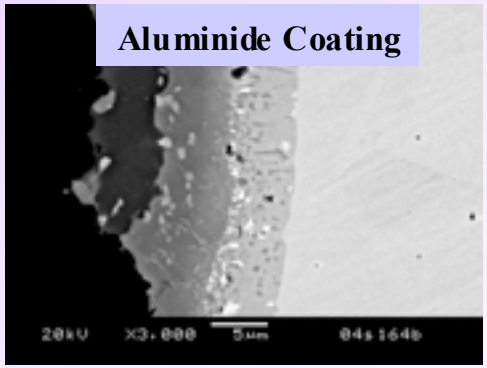
Partners
Dr. Eric Minford; Air Products and Chemicals, Inc.
Dr. Jeff Price; Solar Turbines

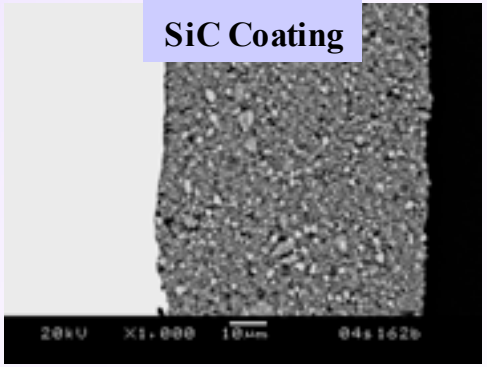
5-year Project 2001-2006, $1.35M

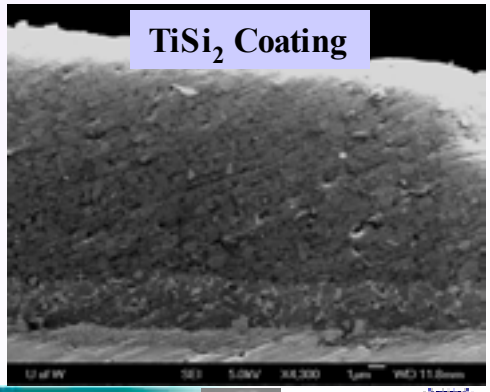
SRI $100K/yr, UW $75K/yr, UCF $50K/yr, PNNL $175K/yr.

Project Summary

- **Goal**
  - Develop low-cost coatings for prevention of high-temperature corrosion of metals and (ceramics).
- **Challenge**
  - Provide protection of high CTE metals and alloys at 700˚C to 1000˚C in oxidizing and reducing environments.
- **Benefits**
  - Energy savings of 160 trillion Btu/year in 2010 assuming a 5% increase in efficiency.
    - Higher temperature operation and use of low-cost alloys.
- **<u>FY06 Activities:</u>**
  - Enhance understanding of coating and coating-substrate interactions.
  - Measure interfacial mechanical properties.
  - Testing of coatings under realistic conditions.
  - Development of commercialization plans.
  - Pursue additional intellectual property.







Barrier-Pathway Approach

- **Barrier**
  - Lack of adequate coatings to prevent carburization of steels in steam-reformer environments.
- **Pathway**
  - Low-cost, paintable, polymer-based coatings.
    - Corrosion resistant ceramic coatings based on SiC and $TiSi_2$.
    - Aluminide diffusion coatings that are Si-free.
- **Critical Metrics**
  - Survive processing at 800-1000˚C on high CTE steels.
    - Thermal cycling (10x) to 800˚C.
    - 1000 h at operating conditions (temperature and environment).
- **Benefits** (based on 5% increase in efficiency where metallic components under metal-dusting conditions are used)
  - Energy savings of 160 trillion Btu/yr.
  - Savings of 3.8 MMTCE.

Project Highlights and Accomplishments

(2004-May 05)

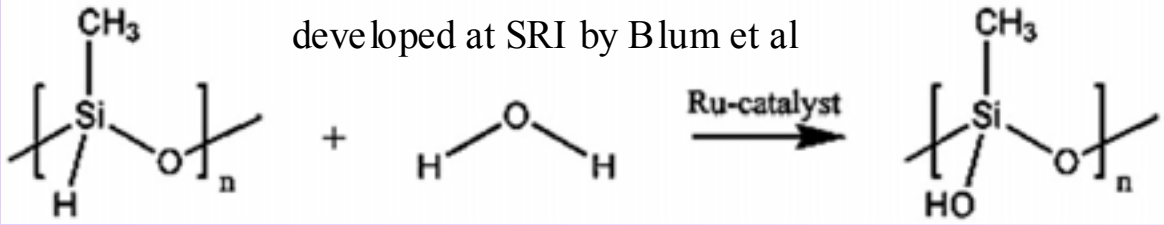
- **A novel, diffusion aluminide coating process has been developed.**
  - **No hot-dipping, pack cementation, or fluidized bed CDV.**
  - **Coating is free of Si which can be a potential problem with some catalytic beds.**
- **Two ceramic coatings have been optimized (SiC filled at PNNL and $TiSi_2$ filled at UW) that survive 10-cycles to 800˚C on 316SS and 100 h at 800˚C.**
  - **These are novel compliant coatings analogous to thermal barrier coatings.**
  - **SiC coating survives 500 h at 800˚C in air.**
- **A novel 316SS-flake filled coating is under development at SRI to grade high-CTE metals to ceramic coatings.**
- **Specimens have been coated for Air Products testing.**
  - **Large coupons (5” x 0.25”) were coated successfully.**

Technical Approach

- Polysiloxane polymers convert to Si-O-C-N, which is corrosion resistant in oxidative and reducing environments.
  - A very inexpensive polymer precursor (PHMS) is used (5-10 $/kg).
  - PHMS chemistry is robust for organic attachments and curing reagents that can be used to control the final coating chemistry.
  - Reactive and inert metal/ceramic fillers to accommodate differential shrinkage, constrained sintering stresses, and thermal expansion.
  - Multilayer coatings for graded CTE and specific protection in a desired environment.
- Coating processing is simple and low-cost.
  - Ceramic coatings and diffusion aluminides have similar processing.
  - Coating application is by painting: dipping, brushing, spraying.
- Coating characterization and testing.
  - Microstructural and chemical.
  - Mechanical Testing (Adhesion).
  - Thermal cycling and high temperature exposure in oxidizing environment.
  - Exposure testing under use conditions

Materials

Polymer (matrix) Poly(hydromethylsiloxane) PHMS



$$PHMS + H_2O + Air \xrightarrow{\text{transitionmetal catalyst}} [Si\text{-}O]_n \xrightarrow{\text{pyrolysis in air to } 800^oC} Si-O-C$$

Liquid polymer, low cost (byproduct of silicone RTV manufacturing), easily modified, high ceramic yield (85%)

Filler (reactive and inert)

To control the shrinkage during processing, thermal expansion coefficient, and known to improve metal-dusting

Containing Ti, Si, Al and Cr (Cr ruled out after consultation with Air Products due to adverse reaction with SMR catalysts)

Portfolio of Coatings

- Al/Alumina powder mixtures
  - Approximately 40 to 60 v/o powder loadings (Al/Alumina equal ratio)
  - Al-flake, 1-2 µm alumina powders.
  - Alumina nanopowders.
- SiC powder
  - 0.7 µm α-SiC powder at 40 to 60 v/o loading.
- $TiSi_2$ powder mixtures
  - Binary metal powders attrition milled to <0.5 µm and 30 v/o loading.
- Stainless steel powder mixtures and multilayer coatings.
  - 316SS flake, 30-50 µm, 40 to 60 v/o.

Simple and similar coating process

- Mix powders, polymer, solvents in roller-mill.
- Dip, spray, paint on substrates.
- Pyrolyze at 800˚C to 1000˚C in air, nitrogen, or argon.

Coating Application

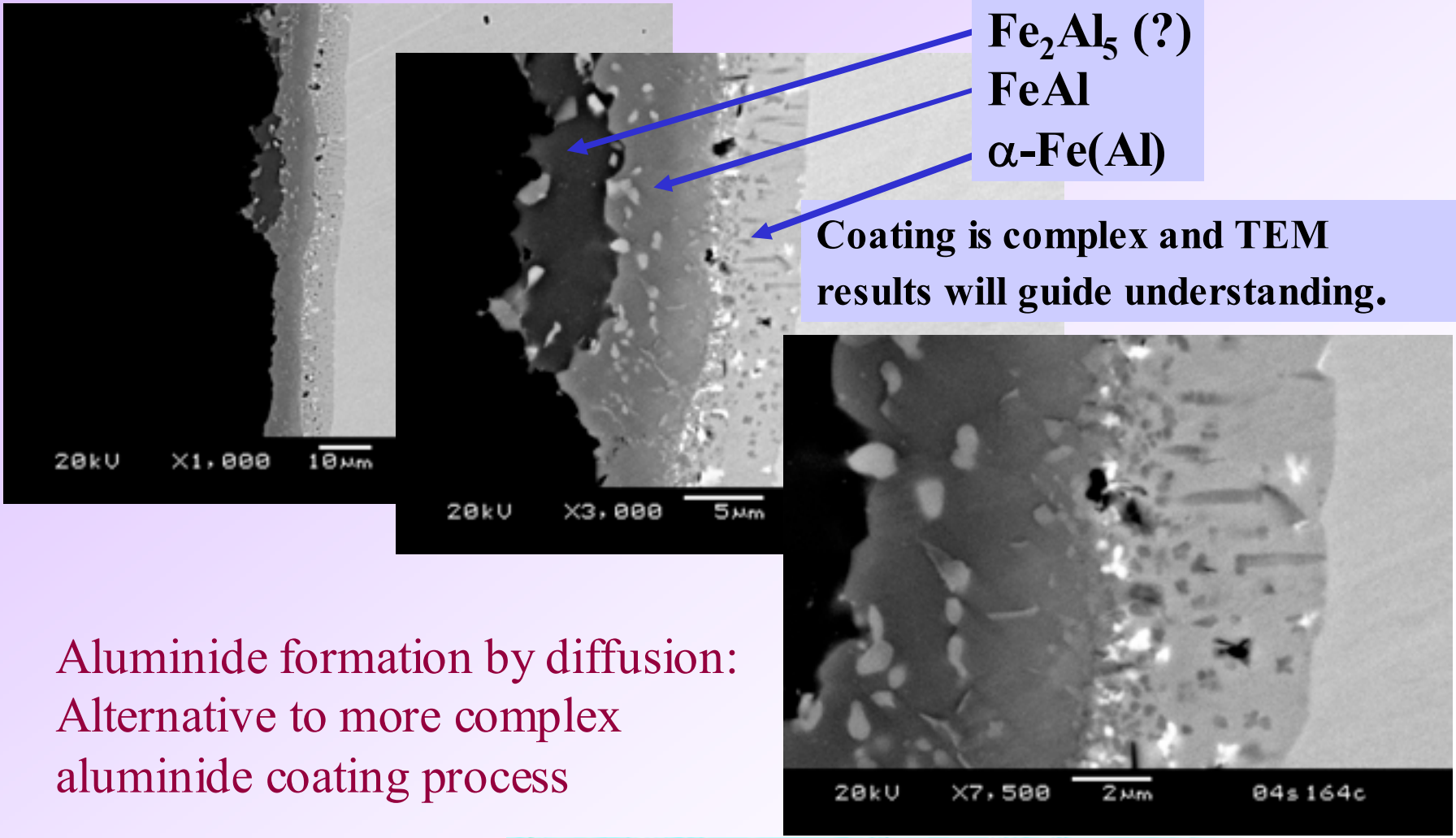
Polymer/filler slurry can be applied like a paint in air at ambient conditions: Dipping, spraying, painting.

Spraying is performed in a hood using compressed air and thinned slurry. Thinning uses same solvent as is used to control viscosity for dipping but requires 2X solvent for spraying.

Summary of Results for Coatings on Steel (316SS)

- Al/Al_2O_3 coatings react to from FeAl regions on steels.
  - Novel slurry-based diffusion aluminide coatings.
  - Forms FeAl on 316SS. Outer skin of alumina.
  - Extremely adherent and protective.
- SiC coatings adherent and continuous.
  - Compliant, granular coating.
  - Survives 500h at 800˚C and repeated thermal cycling to 800˚C.
  - Grows protective silica scale underneath granular coating.
- $TiSi_2$ coatings adherent and continuous.
  - $TiSi_2$ reacts to form TiO_2 and SiO_2 in the coating.
  - Survives repeated thermal cycling to 800˚C.
  - Compliant coatings that grows protective oxide scale under the coating
- Stainless steel flake coatings are adherent as underlayer.
  - Provide CTE match to 316SS and graded underlayer.
  - Adherent coatings to at least 1000˚C in argon and up to 800˚C in air.

Cross-section SEM of Diffusion Aluminide Coatings



Fe_2Al_5 (?)
FeAl
α-Fe(Al)

Coating is complex and TEM results will guide understanding.

Aluminide formation by diffusion: Alternative to more complex aluminide coating process

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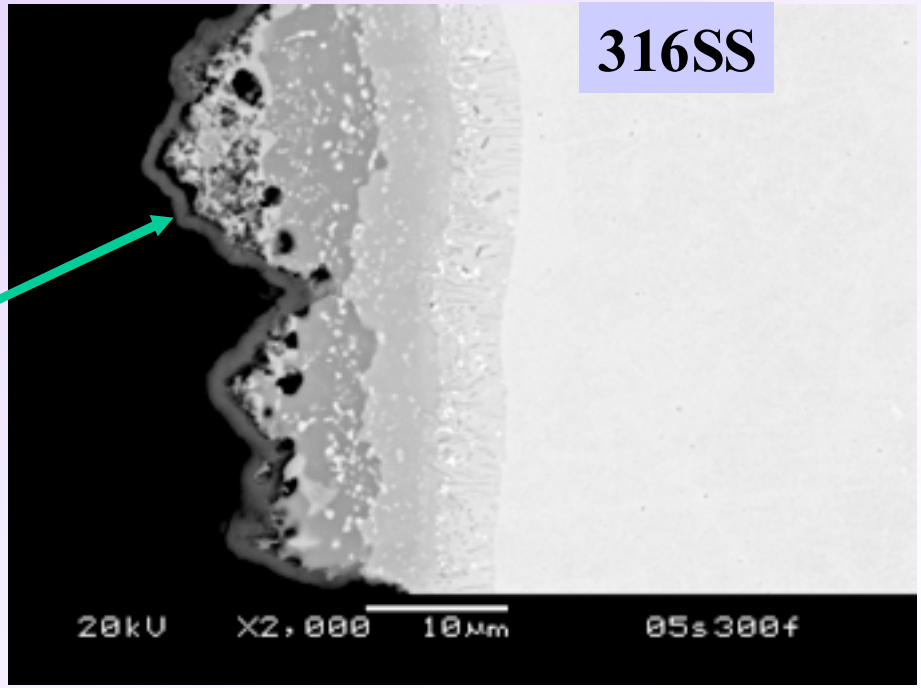
Protective Oxide Formation on Diffusion Aluminide Coatings

Processing in nitrogen followed by air processing can allow alumina skin to form on surface.



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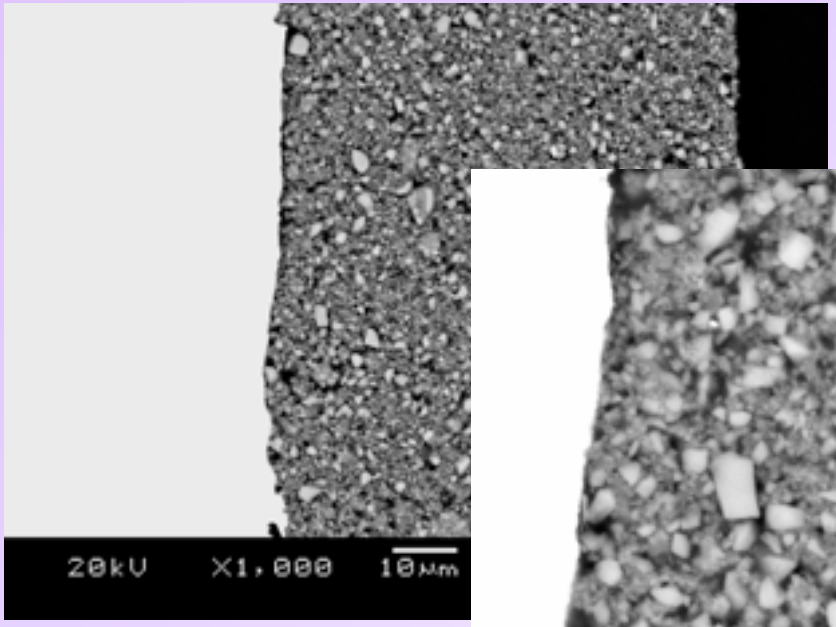
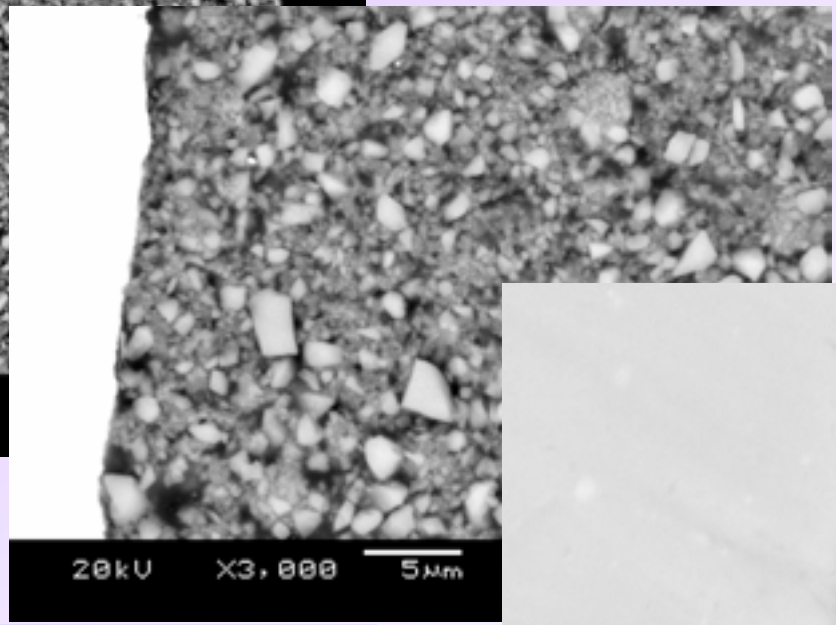
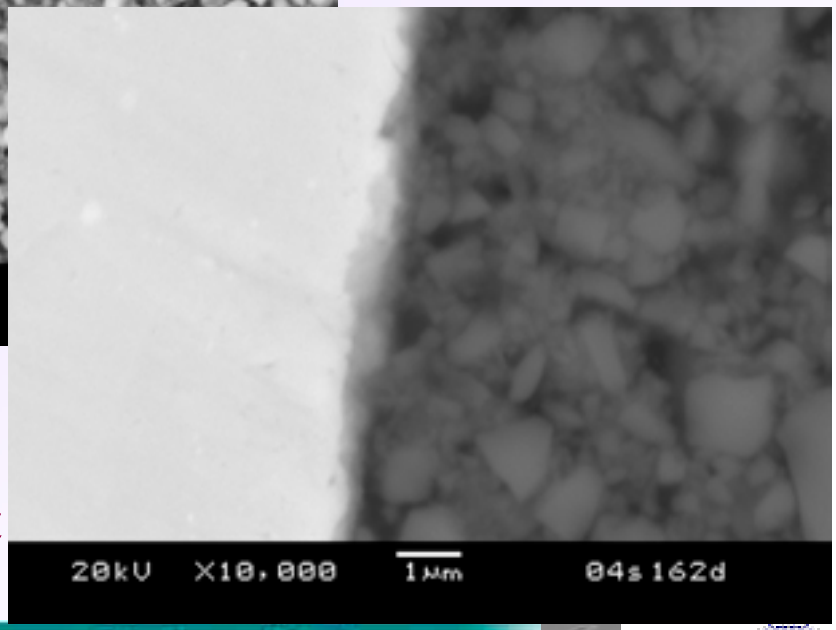
SiC-filled Coatings





SiC cross-section views



SiC particles in glassy matrix

Coating is thick, uniform, and adherent

SiC-filled Coatings Exposure Testing: 800˚C-100 h.

Pre Exposure

SiC+5% Nano-SiC

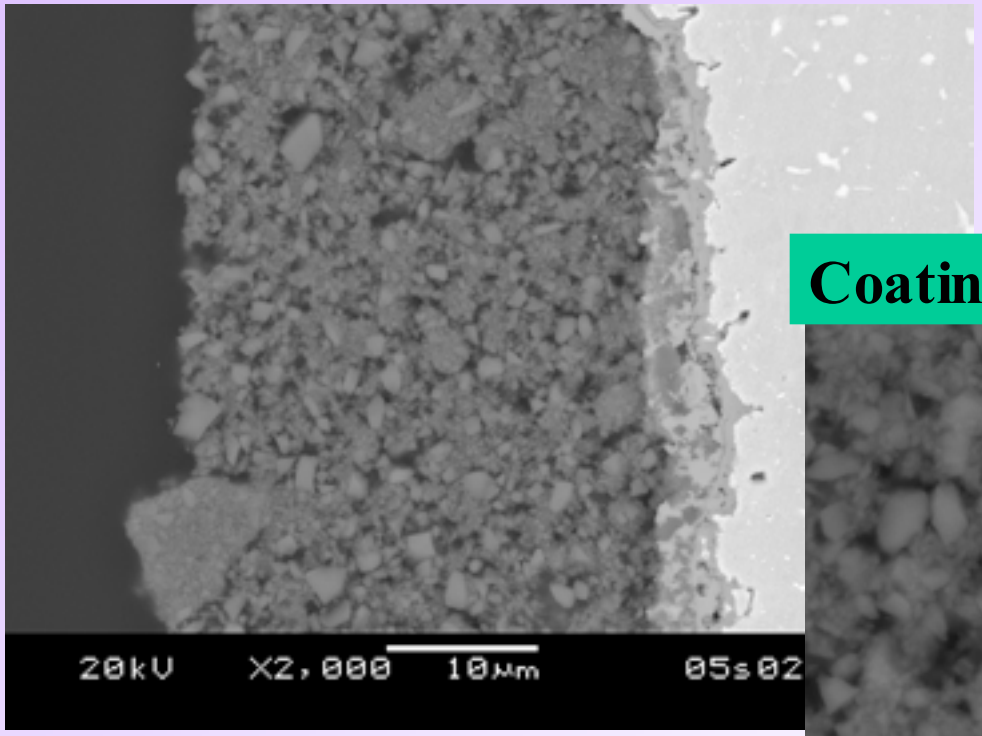
316SS dipped

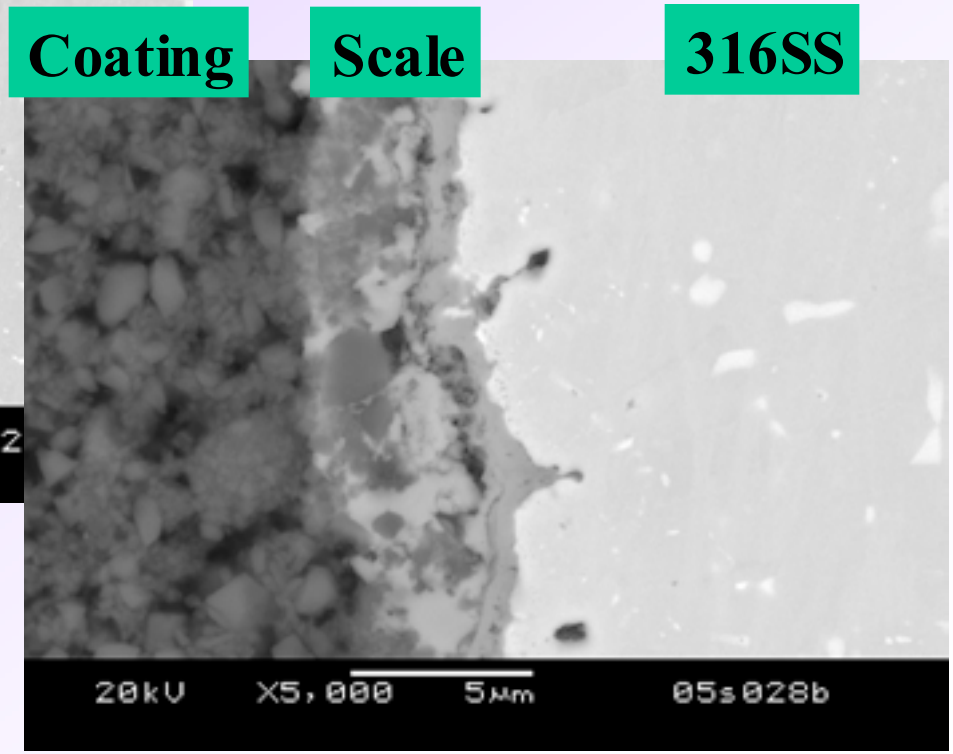
Post Exposure

All coatings survived except the bimodal SiC

Microstructure of SiC-filled Coatings (post-exposure)

800˚C, 100 hours, air.





Growth of oxide scale under the coating (analogous to thermally grown oxide in TBCs)

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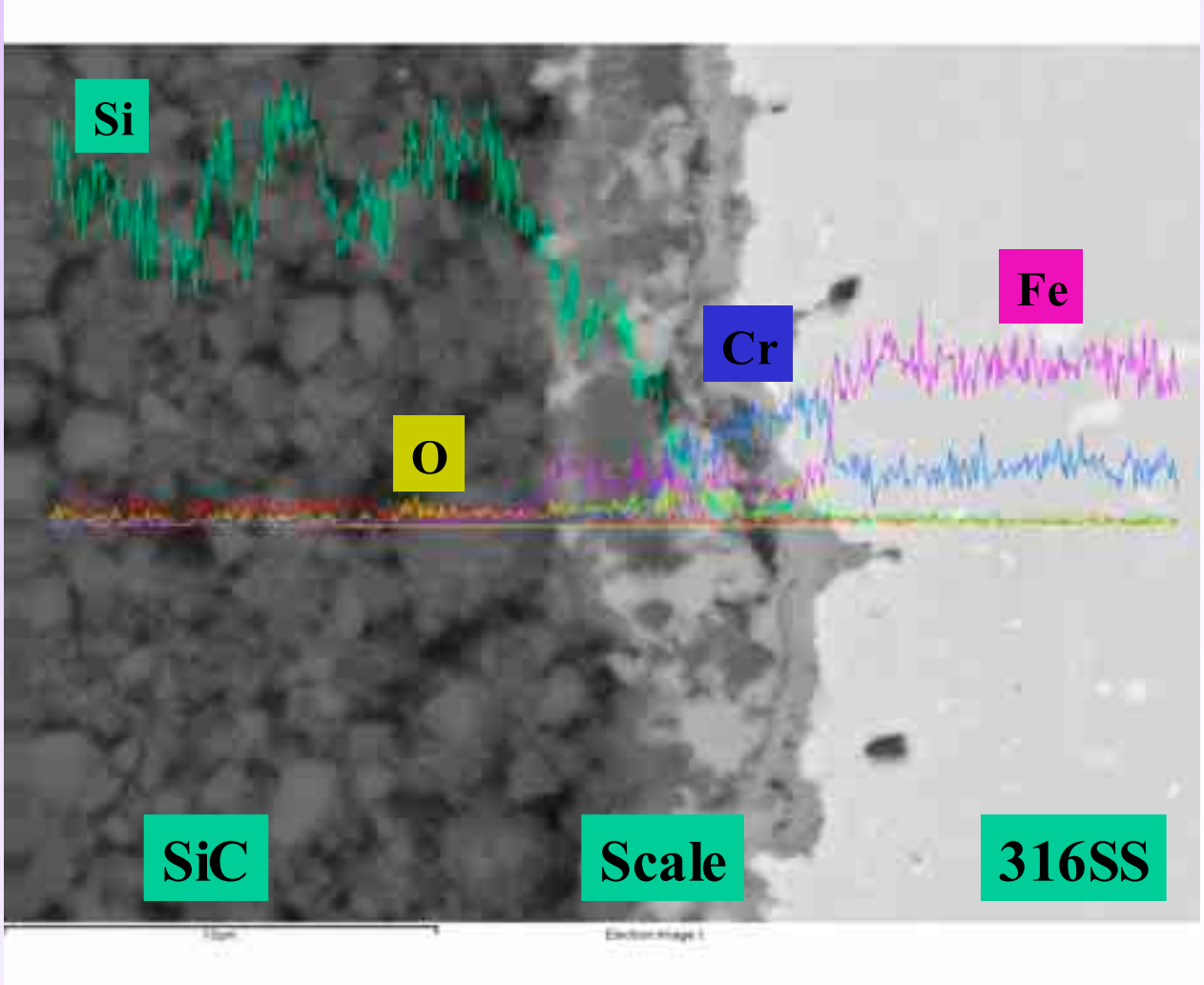
Elemental Analysis of Exposed Coatings

800˚C, 100 hours in air



- ❖Cr enrichment in the scale
- ❖Fe diffusion in the scale
- ❖No Si diffusion into the metal

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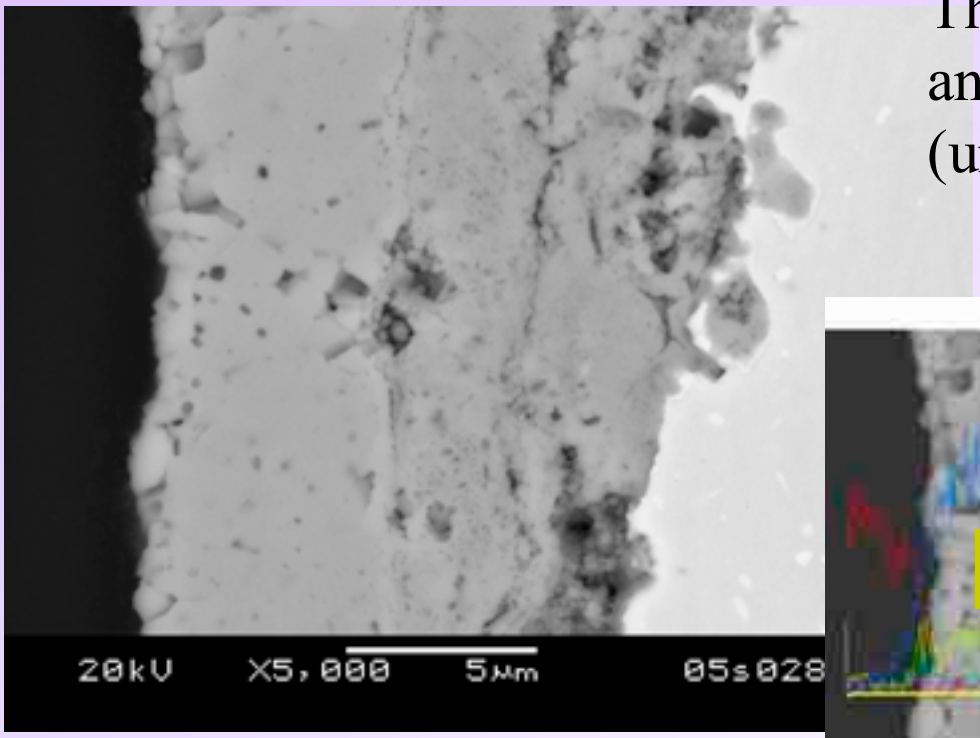
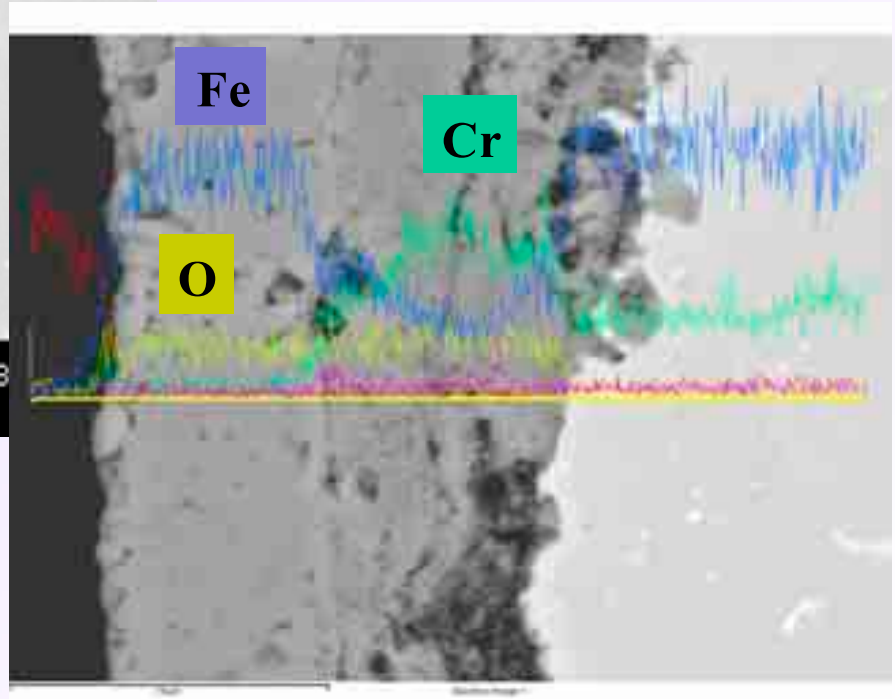
Oxidation of Bare Metal (800°C, 100 hours in air)



Thick oxide scale is rich in Cr and Fe
(undesirable)



Coating is protective in oxidizing environment

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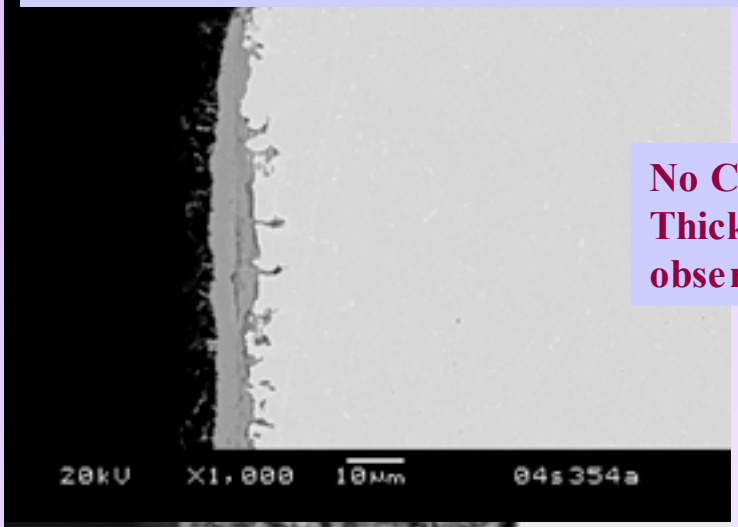
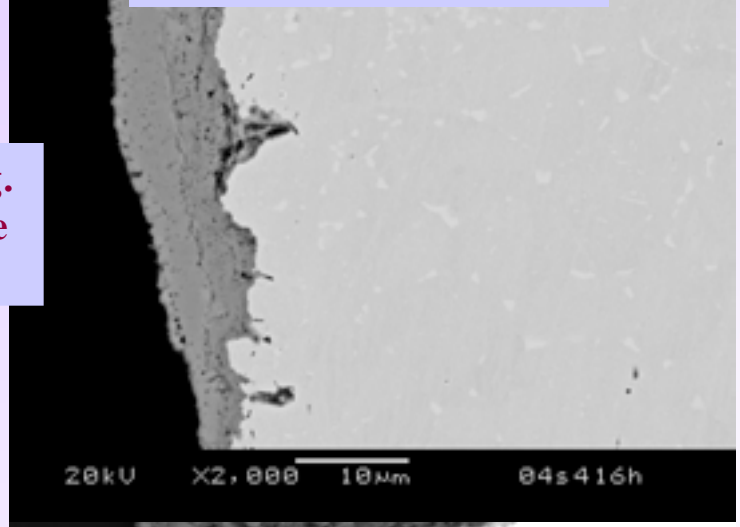
Cyclic and Static Oxidation Testing: SiC-filled Coatings

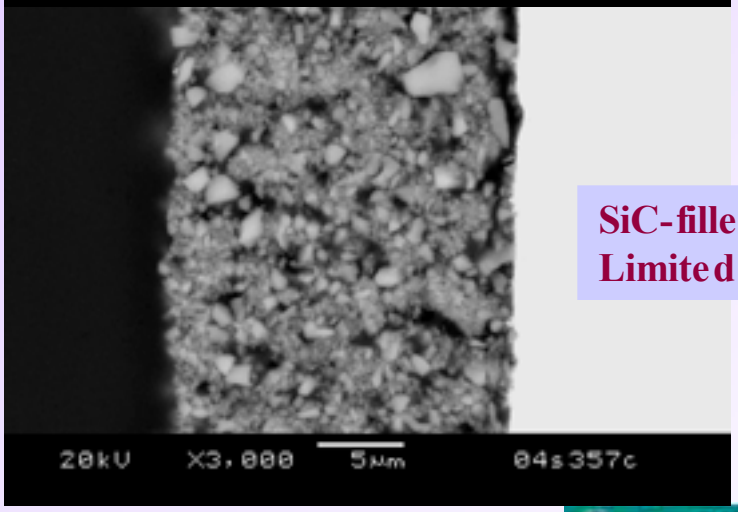
5 Cycles, 800˚C (1 h hold), Air

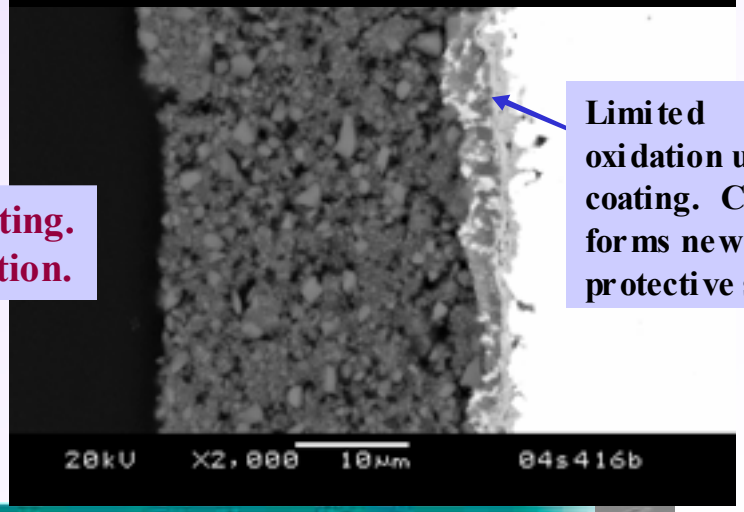
100 h, 800˚C, Air





No Coating. Thick oxide observed.

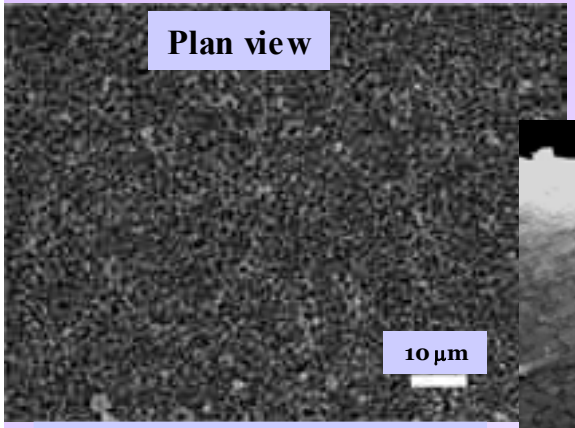


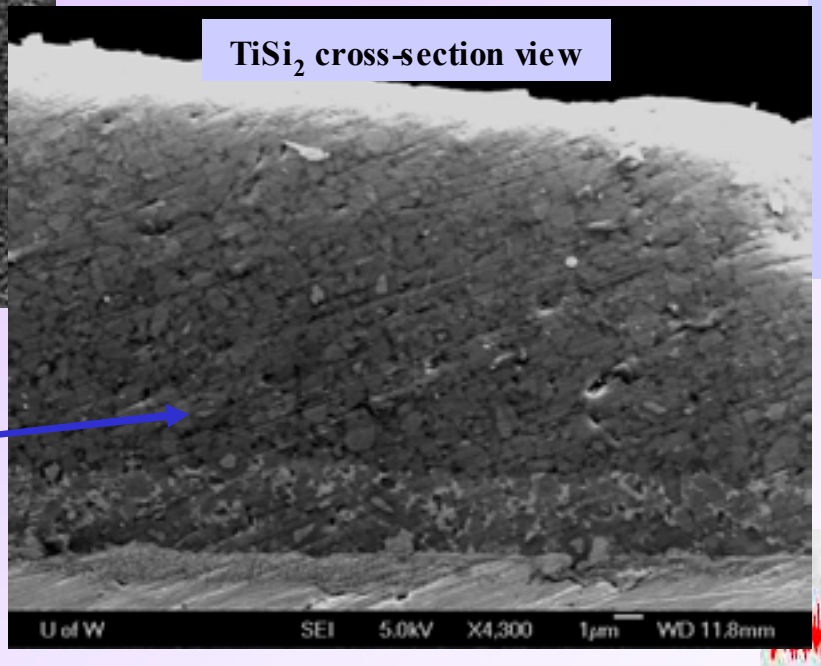


SiC-filled Coating. Limited oxidation.

Limited oxidation under coating. Coating forms new protective scale.

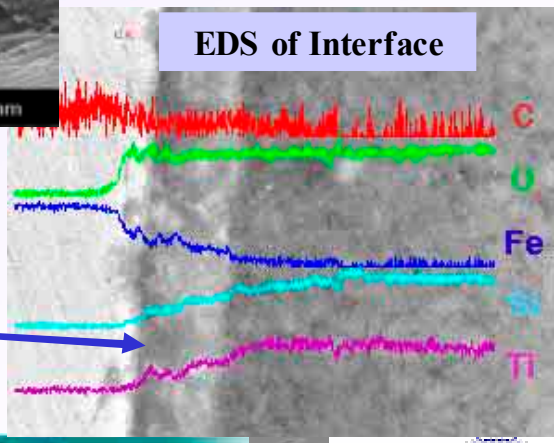
$TiSi_2$-filled Coatings





- 10-12 µm thick coating.
- Good adherence to metal.

- $TiSi_2$ particles converted to oxide in glassy matrix.



- 2-3 µm diffusion oxide layer seen between coatings and substrate (rich in Ti, Si and Fe)

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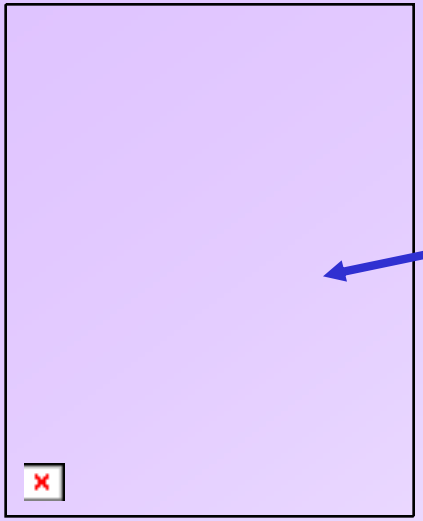
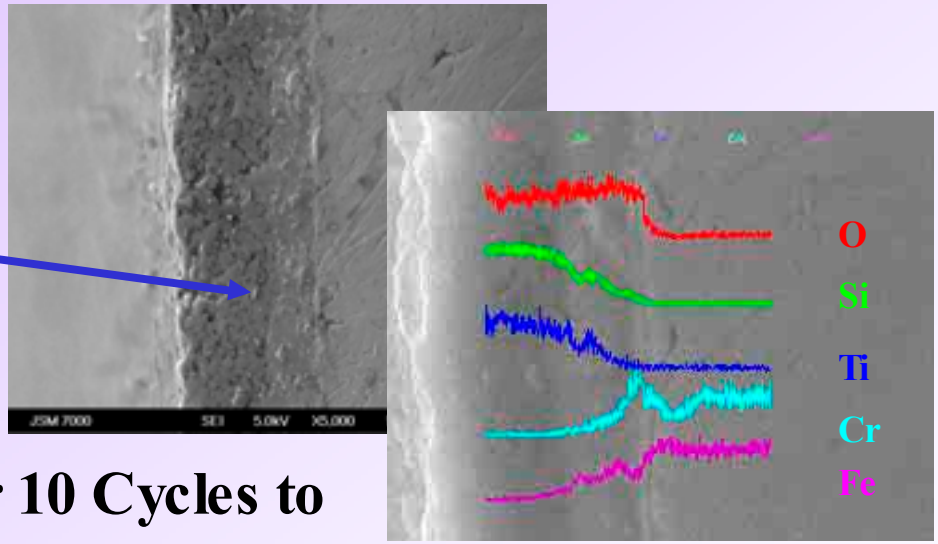
Cyclic Oxidation Test on $TiSi_2$-filled Coatings



After Pyrolysis to 800˚C, Air

Oxidation Layer



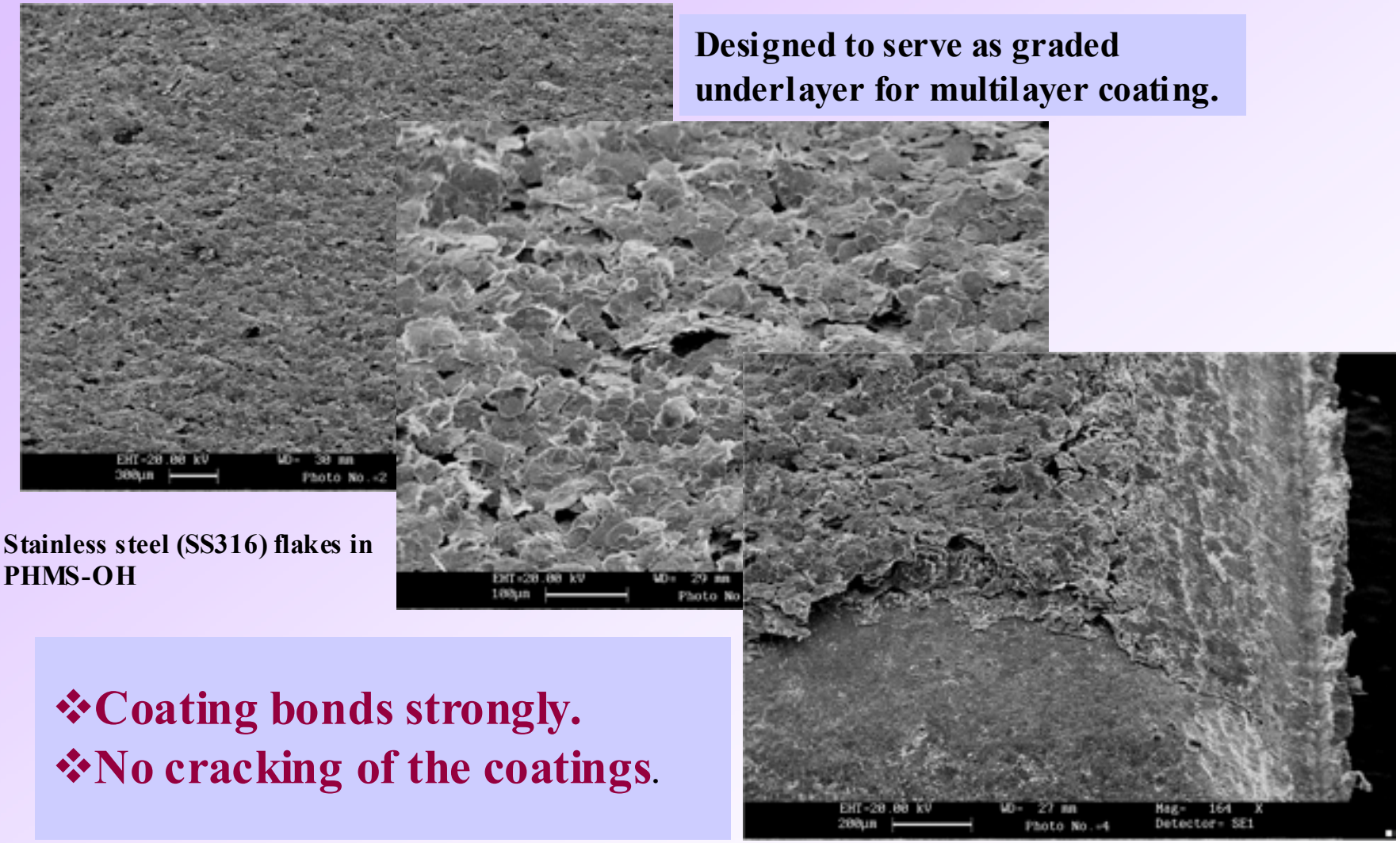
After 10 Cycles to 800˚C, Air, 10ºC/min

10 μm

- ❖No significant increase in oxygen observed at steel interface
- ❖Despite porosity, coating is protective
- ❖Behavior very similar to SiC-filled coating

Both $TiSi_2$ and SiC-filled coatings are complaint: possible reason for their delamination resistance (analogous to TBCs)

316SS-filled Coatings



Designed to serve as graded underlayer for multilayer coating.

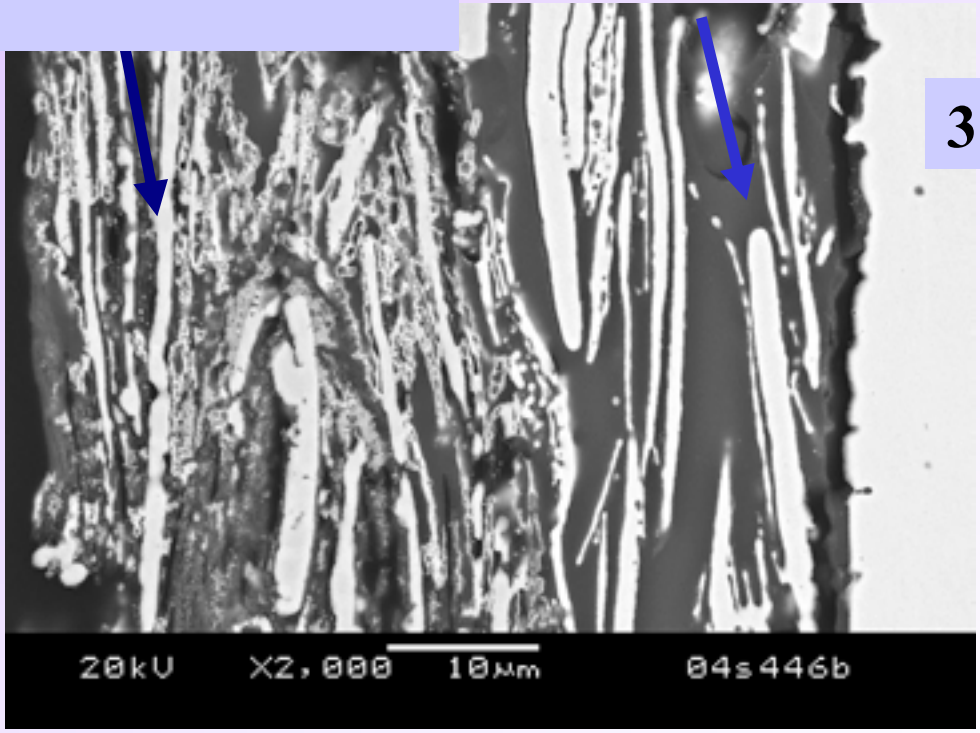
Stainless steel (SS316) flakes in PHMS-OH

- **Coating bonds strongly.**
- **No cracking of the coatings.**

Two-layer Coatings

Second layer: 316SS flakes and Al flakes in PHMS-OH; 1000˚C in Argon

First layer: 316SS flakes in PHMS-OH; 1000˚C in Argon



316SS

The first layer for expansion match with metal; the second layer to grow protective oxide

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Plans for FY 06

- **Work with industrial partner to insure that coatings are tested and evaluated properly.**
  - Complete oxidation and cyclic exposure testing.
  - Air Products to test coatings in SMR environment (simulated).
- **Optimize topcoat layer for 316SS-filled coating underlayer.**
- **Characterize film and interfacial mechanical properties.**
- **Enhance understanding of coating, coating-substrate interactions and its behavior under test conditions.**
- **Publish findings and protect IP.**
- **Continue on commercialization path.**

Simulated SMR Test Coupons for Air Products

SiC

Aluminide

Testing configuration

Commercialization Plan

Three Steps

I. Work with Air Products to evaluate coatings for methane reformer (ongoing).

II. With Air Products identify the best strategy to produce coated components for methane reformer (possibilities: licensing to Air Products, working with their suppliers).

III. Other uses for the coatings (ongoing).

- Evaluate coatings with other industrial partners (current plans with Solar Turbines)
- Discuss coatings with coating manufacturers (Metal Coatings)

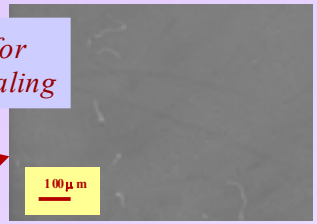
Commercialization Step III
Versatile, Robust Coatings at Low Cost

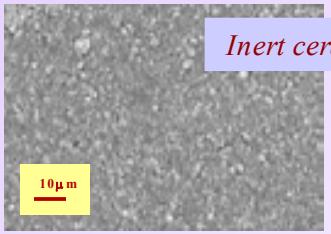
PHMS-OH
7-14 $/Kg

PHMS
5-10 $/Kg

RO-PHMS-OH
5-10 $/Kg

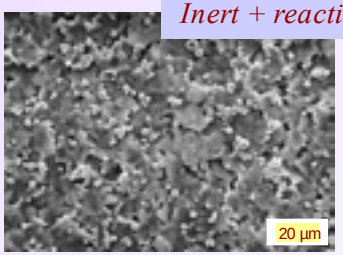
Unfilled thin films for planarization and sealing



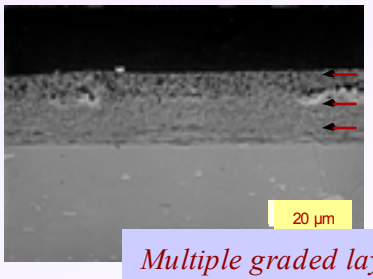


Inert ceramic filled

Inert + reactive filled



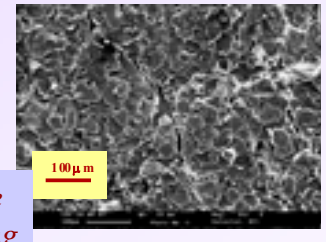
Attributes
Low cost "paints"
High temperature (>800°C)
Corrosion and chemical resistance
Large and complex surface area



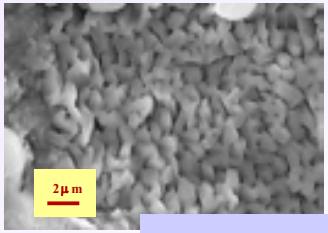
Multiple graded layers

Ceramic powder fillers
3-20 $/Kg

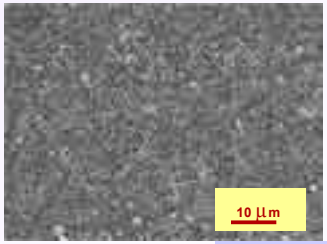
Reactive fillers
3-20 $/Kg



SS composite CTE matching



FeAl diffusion coatings



Reactive metal filled

Broad Range of Possible Applications

- Hydrogen economy
  - 80% of H_2 volume produced by SMR (Syngas)
  - Air products alone – 35 SMR plants
  - Coal and Biomass gasification plants
    - 160+ plants worldwide; Equivalent to 770,000 oil barrels per day
  - Major uses of Syngas (H_2/CO)in production of ammonia, methanol, and other chemicals.
- Petrochemicals
  - Ethane/propane to Ethylene cracking (pyrolysis)
  - Hydrocracking and hydrotreating plants (also H_2 consumers)
  - Heavier oil to light fuel (growing trend consuming H_2)
- Coal and gas based electrical power
- Many other corrosion resistance applications for steel and stainless steel industrial applications
  - Heat exchangers, engines, pipes, construction materials

Growing volume maturity

Lower H_2/CO ratio
Higher corrosion problem

Received inquiries for potential use in Bio-gas production and use for coating SOFC interconnects

Step III: Broader Commercialization Plan

Discussions with coating producers (focus on those with expertise in liquid based coatings)

e.g. Metal Coatings Corp. and Applied Coatings and Lining, Inc.

Expertise in carbon based polymer on complex shapes

From Metal Coatings Corp.

Summary

- **PHMS precursor plus fillers makes very inexpensive coatings with wide range of control over processing.**
  - **Versatile chemistry for microstructural and chemical tailoring.**
  - **Polymer allows air handling and extremely simple processing (painting, dip-coating, spraying).**
- **Broad range of composite coatings can be formed by simple painting/heating techniques.**
  - **Diffusion-reaction coatings.**
  - **Reactive and inert filler powders.**
  - **Simple heating cycles in nitrogen, argon, or air.**

Summary

- Our advanced composite coatings exhibit the following features:
  - Reactive with metal surfaces (good wetting and adherence).
  - FeAl formation on steels for diffusion aluminide coating.
  - Excellent results obtained on SiC- and $TiSi_2$-filled coatings.
  - Stainless steel composite coating as underlayer shows promise for grading CTE.
- Application of coatings requires little special equipment.
  - Spraying for large area coverage.
  - Slurry dipping for coating internal surfaces.

Thank You