Oxidation Resistant, Cr retaining, Conductive Coatings on Metallic Alloys for SOFC Interconnects

Dr. Vladimir Gorokhovsky
Director of Research and Development
Arcomac Surface Engineering, LLC
Bozeman, MT

In collaboration with: MSU; PNNL; LBNL; and NASA-GRC.

This Program is Supported by DoE/SECA Contract No. DE-FC26-04NT42225

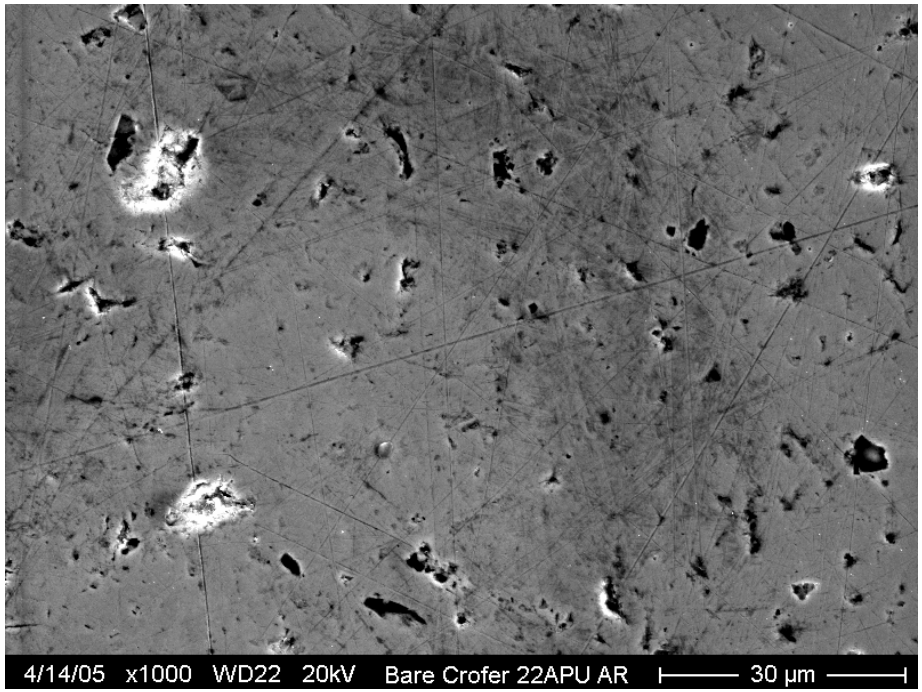
Collaborative Team:

- Arcomac Surface Engineering, LLC
  - Dr. V. Gorokhovksy; Mr. D. VanVorous
- Montana State University
  - Drs. M. Deibert, R. Smith, A. Kayani; Mr. P. Gannon
- PNNL
  - Drs. Z. Yang, J. Stevenson
- NASA-Glenn Research Center
  - Dr. S. Sofie
- LBNL
  - Drs. S. Visco, C. Jacobson, H. Kurokawa

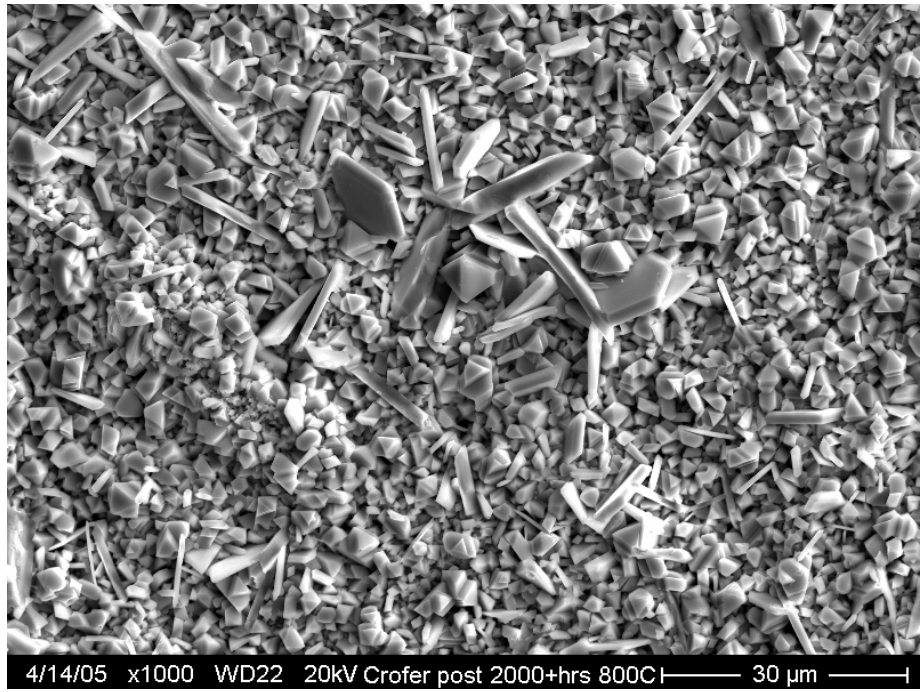
Presentation Outline

- SOFC Metallic Interconnects: Needs in Surface Engineering Technology
- Arcomac's Technical Approach: Dual Segment Multilayer Cermet Coatings by Filtered Arc Assisted Vapor Deposition
- Results and Discussion: Coated vs. Uncoated Crofer 22 APU
- Summary and Path Forward

Uncoated Crofer 22 APU

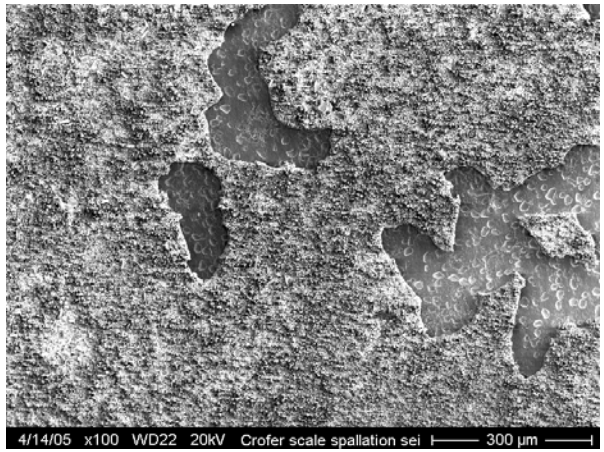


Polished Coupon Surface Before Oxidation Exposure

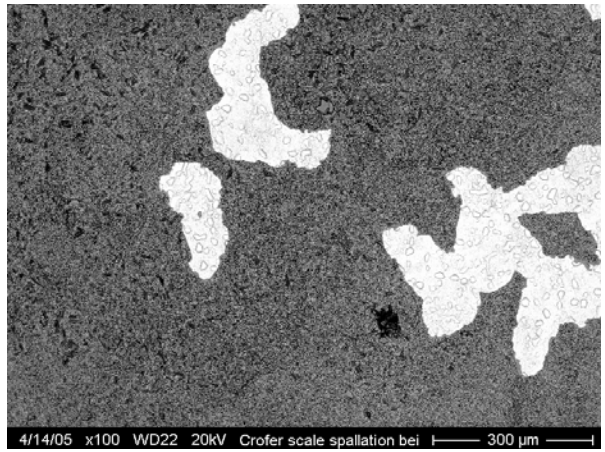


Coupon Surface After 2000+hrs Oxidation at 800C in Air

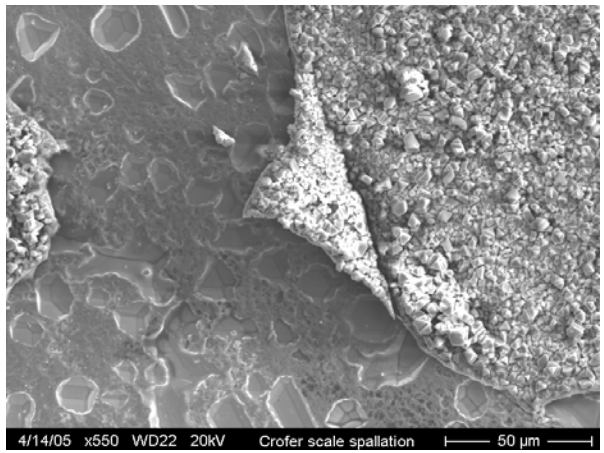
Uncoated Crofer Oxide Scale Spallation

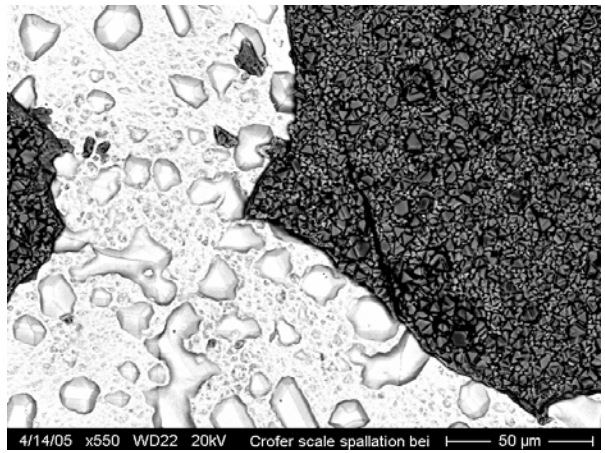


Secondary Electron Images Illustrating Scale Spallation



Backscattered Electron Image Illustrating Scale Spallation, Emphasizing Crofer Substrate

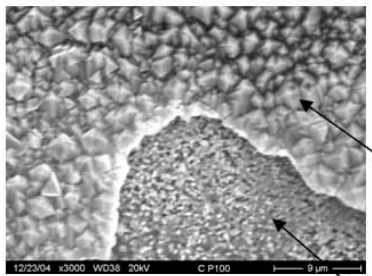


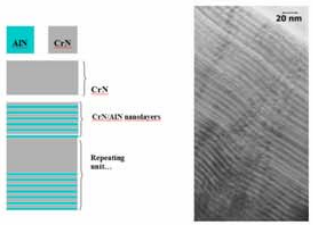


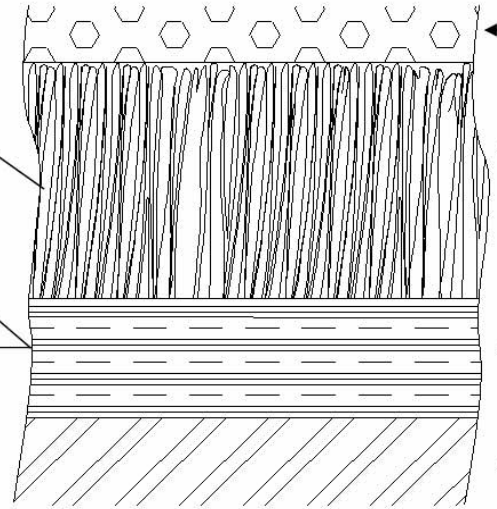
Arcomac's Technical Approach

- **2-Segment Coating Concept:**
  - 1st Segment – nanolaminated CrCoON/AlON (oxidation resistant diffusion barrier, bond coating)
  - 2nd Segment – columnar grain $(Mn,Co)_3O_4$ (electrically conductive, Cr-retaining spinel)
- **Hybrid Surface Engineering Techniques**
  - Coating deposition process combines conventional and advanced evaporation and ionization sources (filtered arc deposition (FAD) and filtered arc-assisted e-beam evaporation physical vapor deposition (FAD-assisted EBPVD))
- **Simulated Performance Evaluation**
  - Testing for SOFC compatibility: HT oxidation; electrical conductivity; and prototypical performance

ASE's Hybrid Coating Concept







SOFC Cathode (e.g. LSF or LSM)

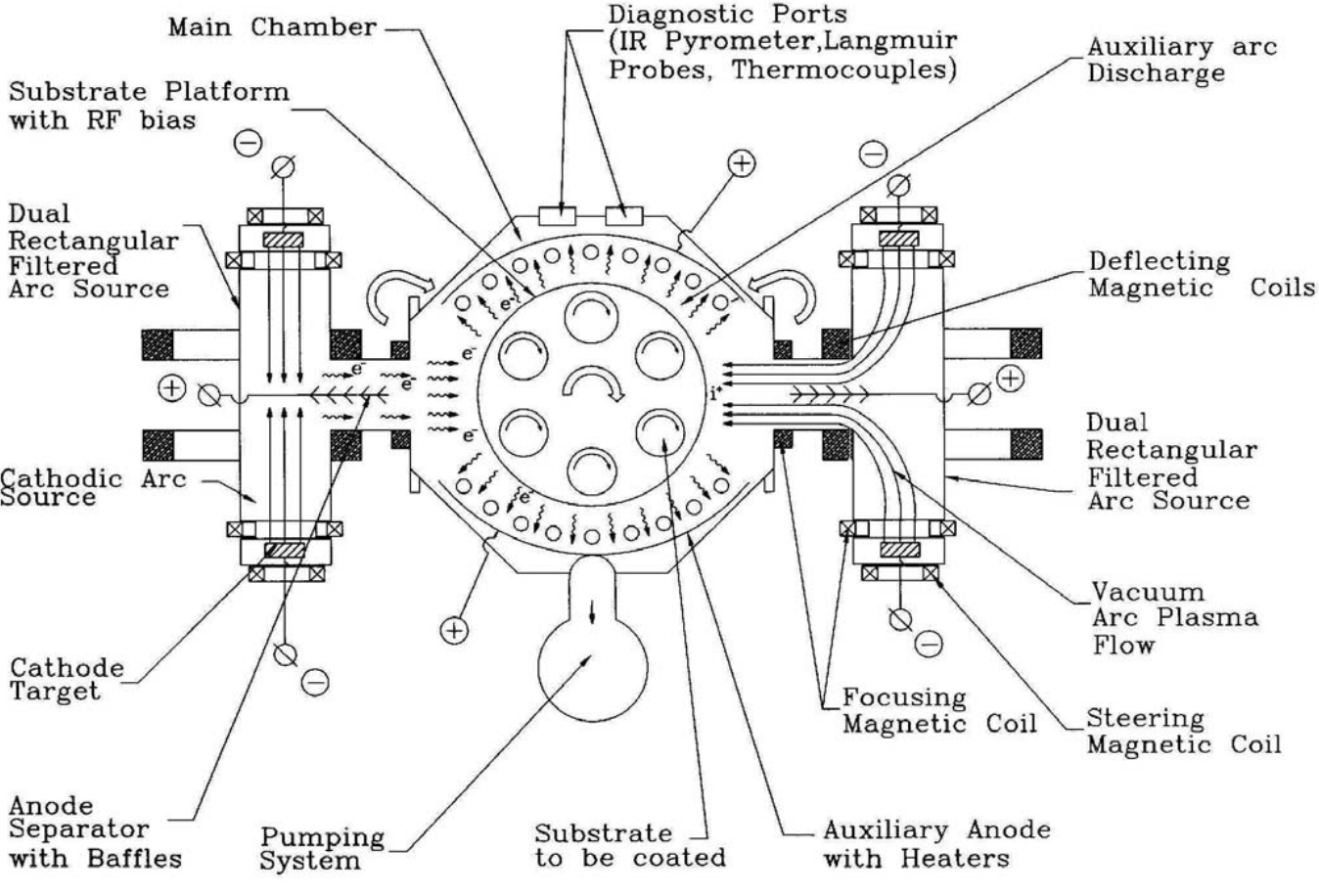
$(Mn,Co)_3O_4$ Columnar FAD assisted EBPVD deposit – electrically conductive and accommodates cathode/interconnect interfacial stresses

CoCrAlON nanolaminated FAD corrosion resistant bond interlayer – improves coating adhesion and blocks O_2 inward diffusion

Metallic Interconnect Substrate, e.g. Crofer 22 APU (Optionally Ion-Nitrided)

Large Area Filtered Arc Deposition (LAFAD™) Technology:

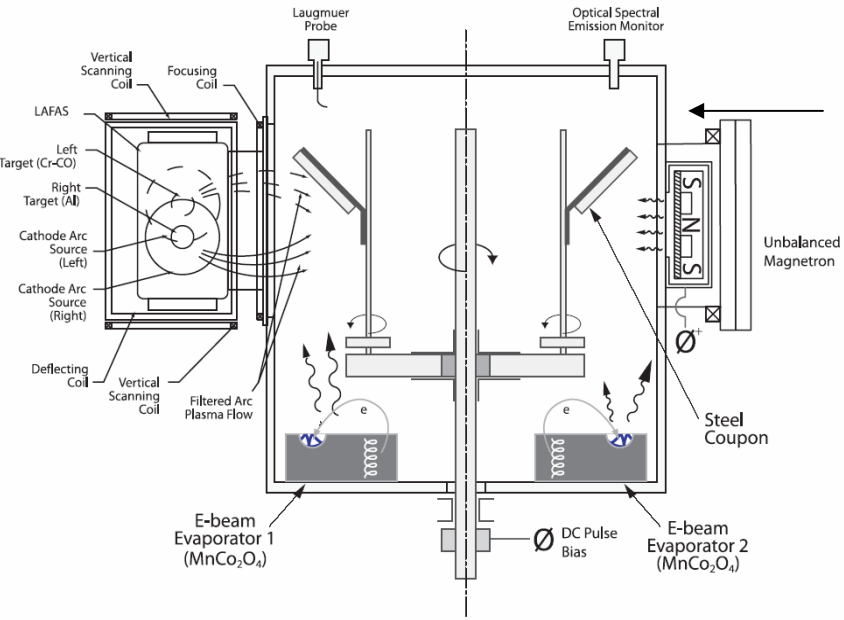
average direct kinetic energy of ions in filtered arc beams ranges from 40 to 200eV



New Generation of PVD Coating Technology: Filtered Arc Plasma Source Ionized Deposition (FAPSID) Surface Engineering Process

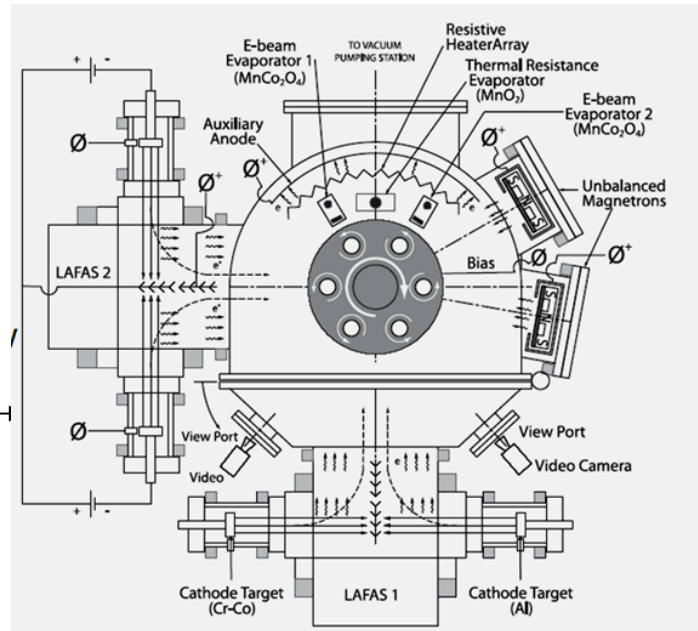
Schematic Illustration of One Embodiment of the FAPSID Process: Arcomac's Hybrid Filtered Arc-Assisted FA/EBPVD Surface Engineering System:

- **Industrial Scale Uniformity and Productivity**
- **Large Area Filtered Arc (LAFAD) CrCoAlON ~1um/hr**
- **Filtered Arc-Assisted FA/EBPVD $(Mn,Co)_3O_4$ ~6um/hr @ 300W EB Power**



Side view

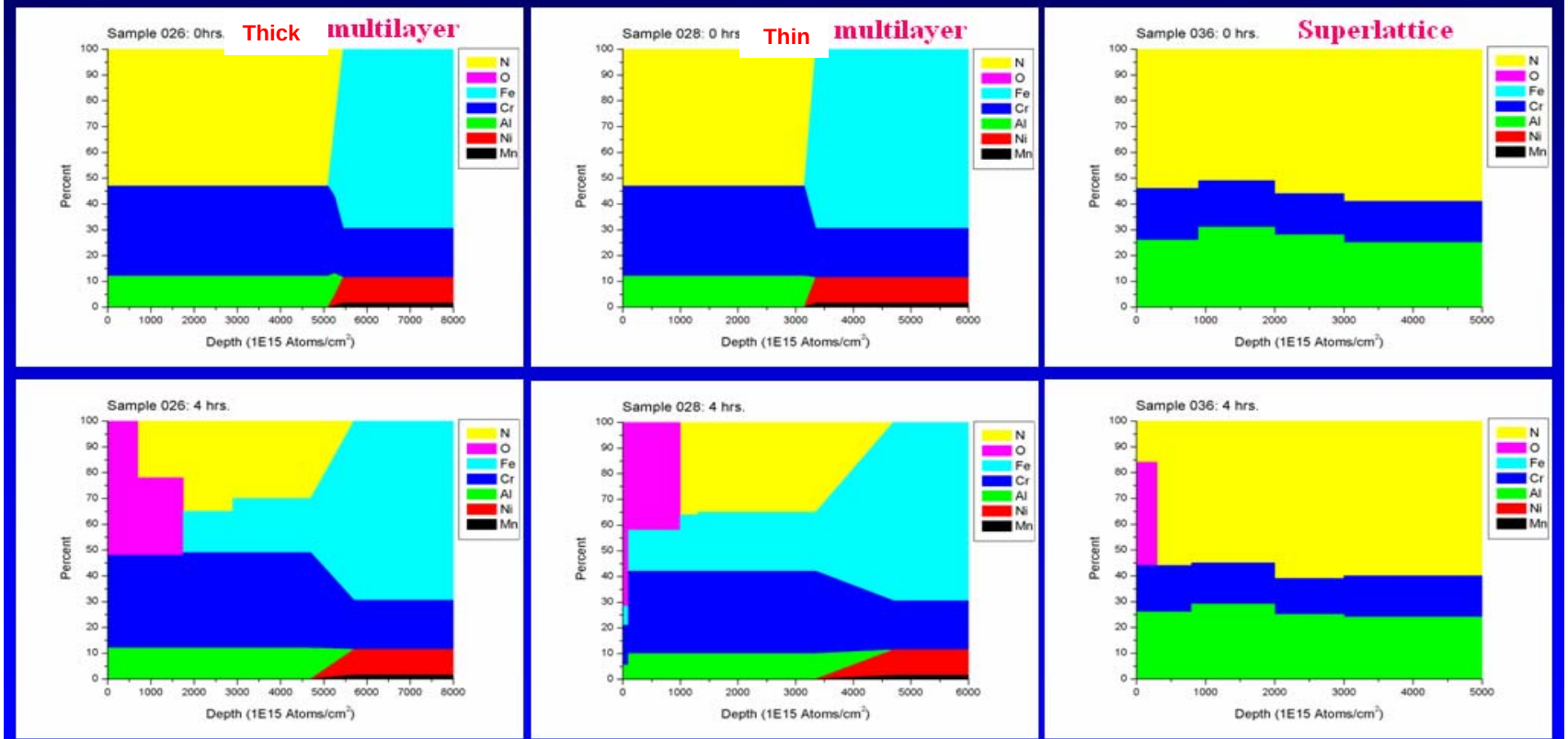
Top view



Advantages of Large Area Filtered Arc-EBPVD Technology:

- Atom – by – Atom Deposition
- Process Produces Defect Free Coatings: no Voids, Porosity or Macroparticles
- High Ionization and Activation of Metal-Gaseous Plasma
- Capable of Mixing Virtually any Composition of Elements in Plasma Flow Prior to Deposition
- Capable of Combinatorial Processes Utilizing any Plasma Assisted PVD and Low Pressure CVD Processes in One Universal Surface Engineering Chamber Layout
- Multi-Phase, Ultra-Fine, Polycrystalline or Amorphous Coating Structure
- Nano-scale Coating Architectures
- Capable of Supporting Duplex and Triplex Plasma Immersion Surface Engineering Processes in One Vacuum Cycle
- Industrial Scale Uniformity and Productivity
- Enhanced Capabilities over Conventional Coating Technologies at Lower Cost
- Environmentally-Friendly, Dry Process with Negligible Hazardous Byproducts

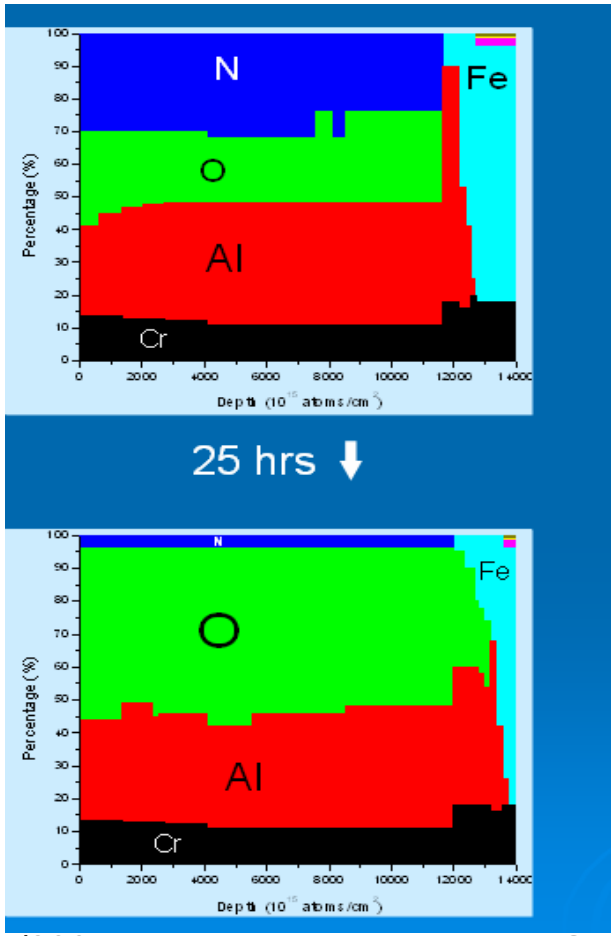
RBS Concentration Profiles: Before(top) after (bottom) 4 hrs @ 800 C in air



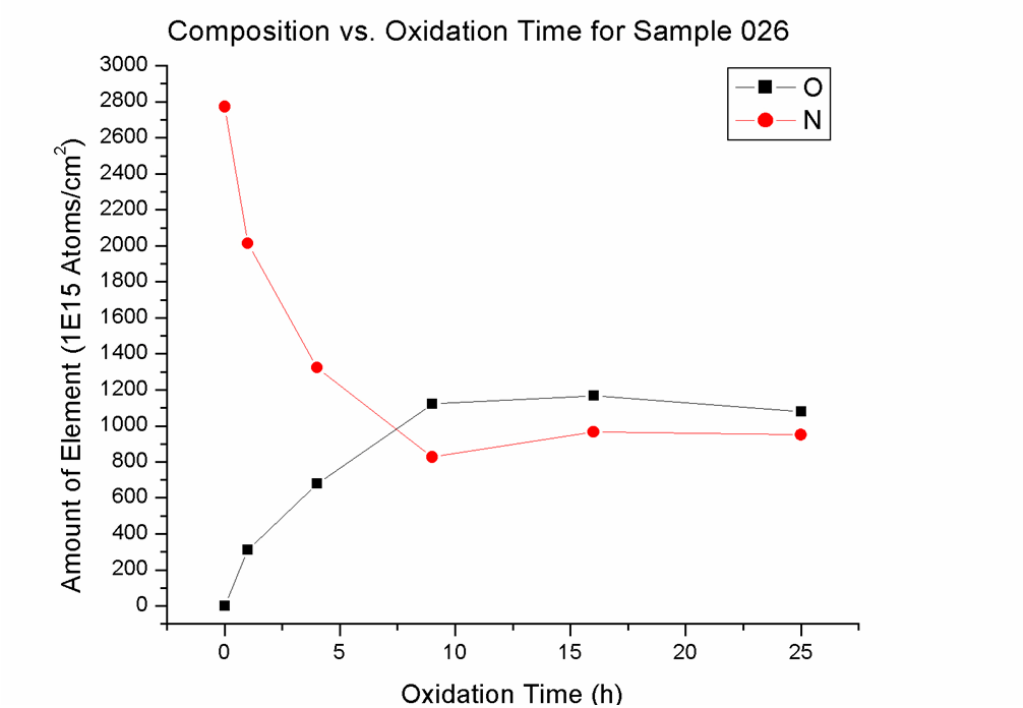
Oxidation kinetics of St.St. with Filtered Arc CrAlN coatings of various architectures

Early Stages of Oxidation by RBS: Control of Oxidation Protection Properties by Varying Coating Composition and Architecture

Filtered Arc CrAlON nanolaminated coating demonstrates retention of its barrier properties during 25hrs of oxidation @ 800C in air

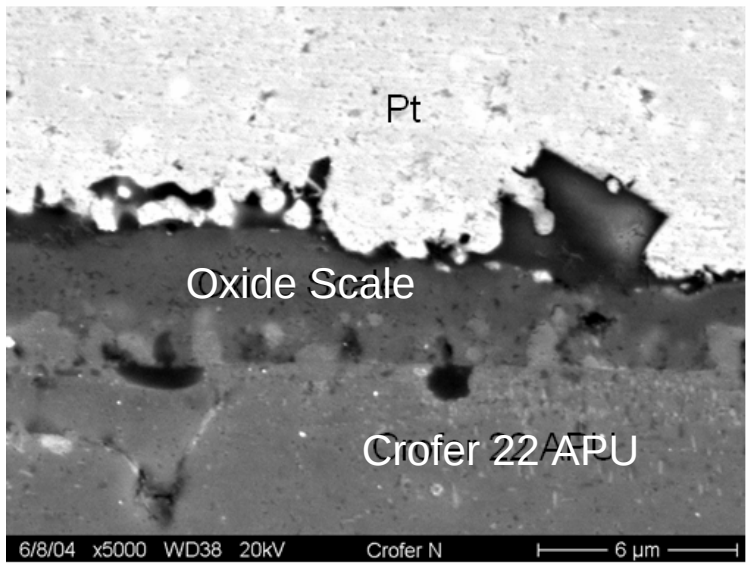


Filtered Arc CrAlN nanolaminated coating does not lose entire N content during 25hrs of oxidation @ 800C in air



SEM Cross-section post ASR Testing

Forming TGO on Uncoated Crofer 22APU after ~750hrs of oxidation

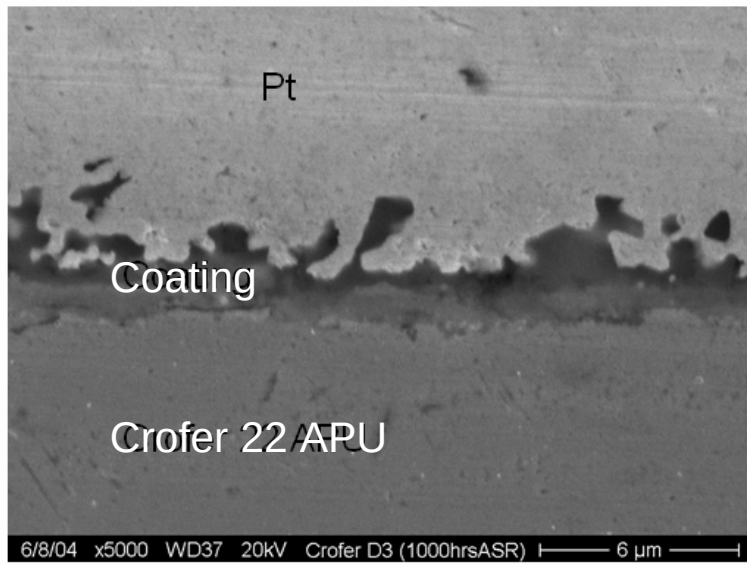


Uncoated Crofer 22APU

Scale ~3-5um

~750 hrs @800°C

Forming TGO on CrAlON Filtered Arc Coated Crofer 22APU after ~1000+ hrs of oxidation

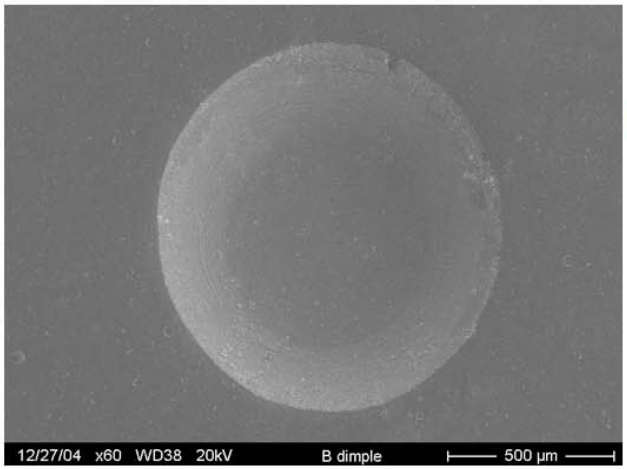


Coated Crofer 22APU

Scale/Coating ~1um

1000+ hrs @800°C

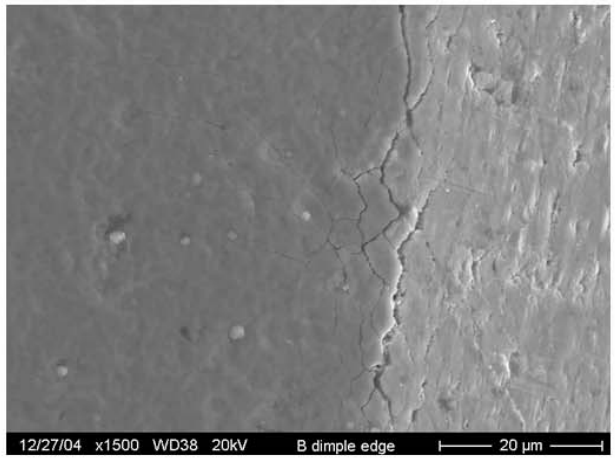
Coating Adhesion Assessment - Rockwell 145kg Indentations

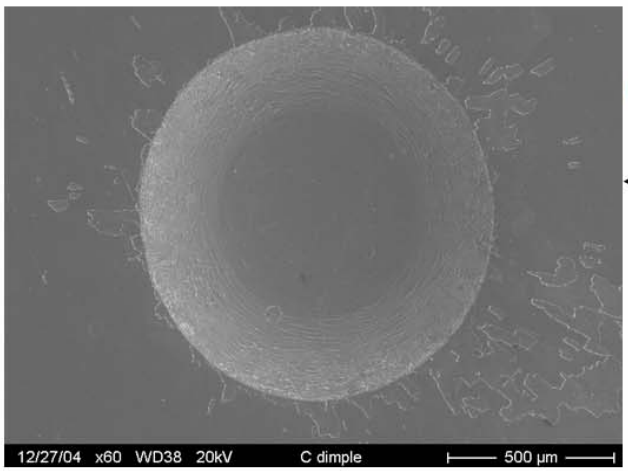


2-Segment Coating

Lower, nanolaminated CrCoON/AlON Bond-Coat with Upper $(Mn,Co)_3O_4$

(Excellent Adhesion)

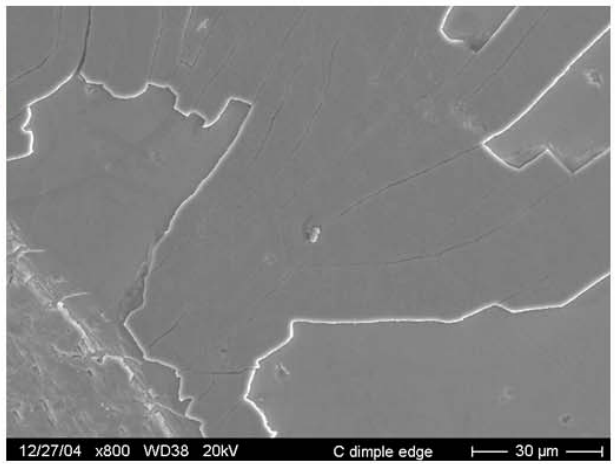




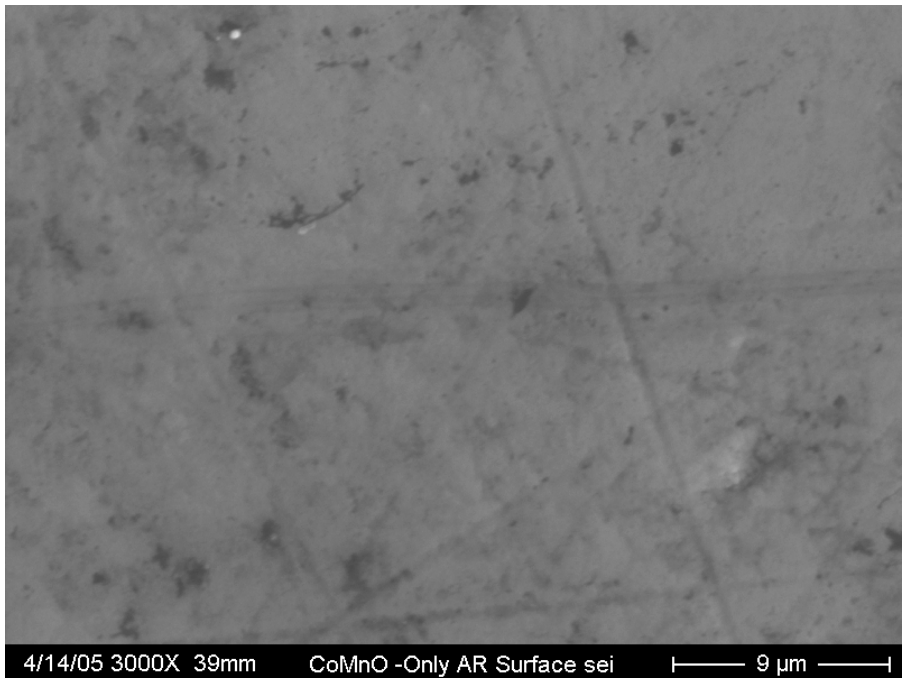
1-Segment Coating

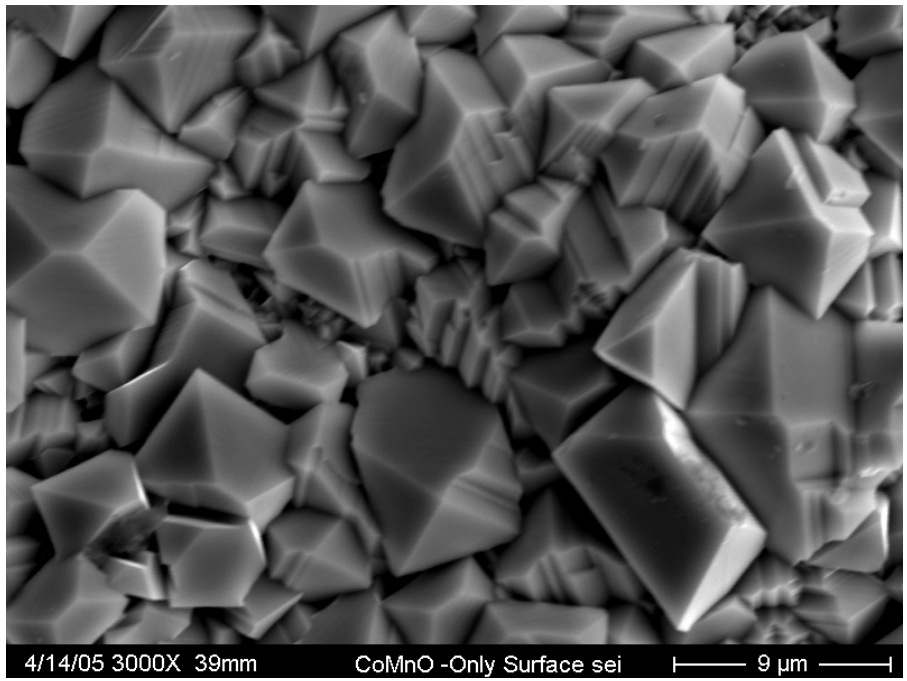
Upper $(Mn,Co)_3O_4$ Only

(Fair Adhesion)



$(Co,Mn)_3O_4$ Single Segment Coating Recrystallization



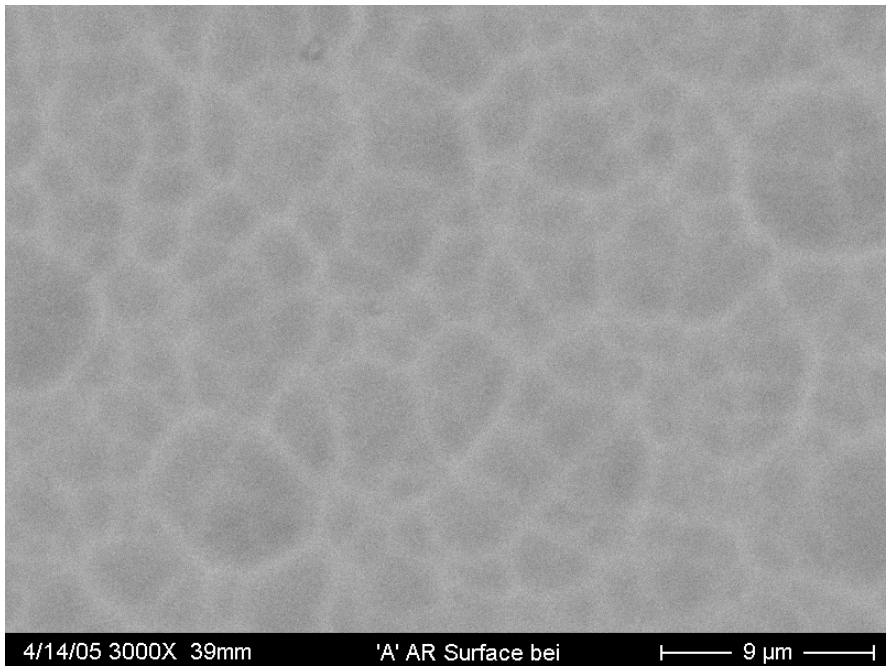


As deposited, amorphous or ultrafine polycrystalline $(Co,Mn)_3O_4$ single layer coating

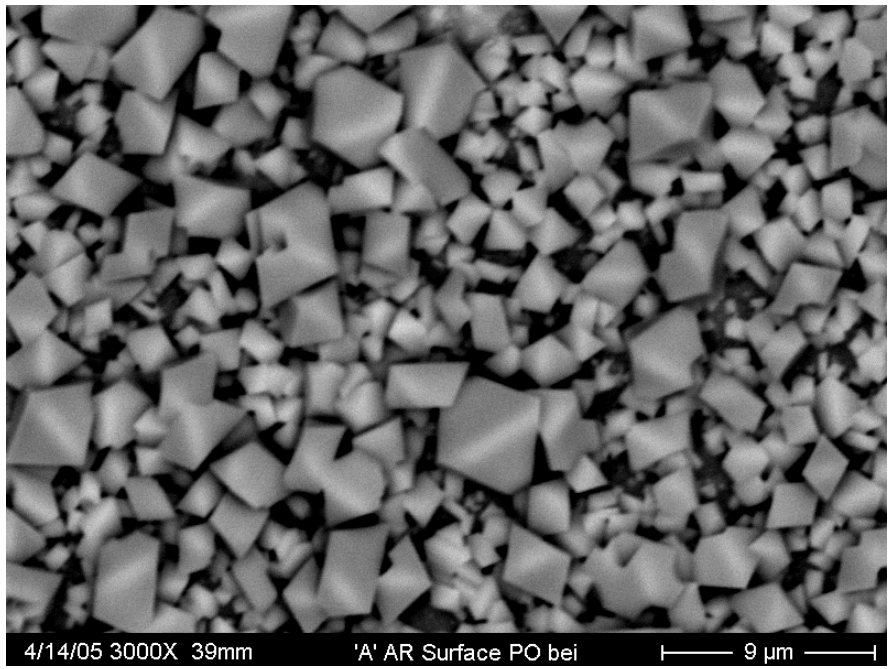
Post 2000+ hrs oxidation, 800C in air, polycrystalline $(Co,Mn)_3O_4$ single layer coating

Surface Composition (EDS) = ~22%Co,Mn, bal. O

CrON/AlON+$(Co,Mn)_3O_4$ Dual Segment Coating Recrystallization

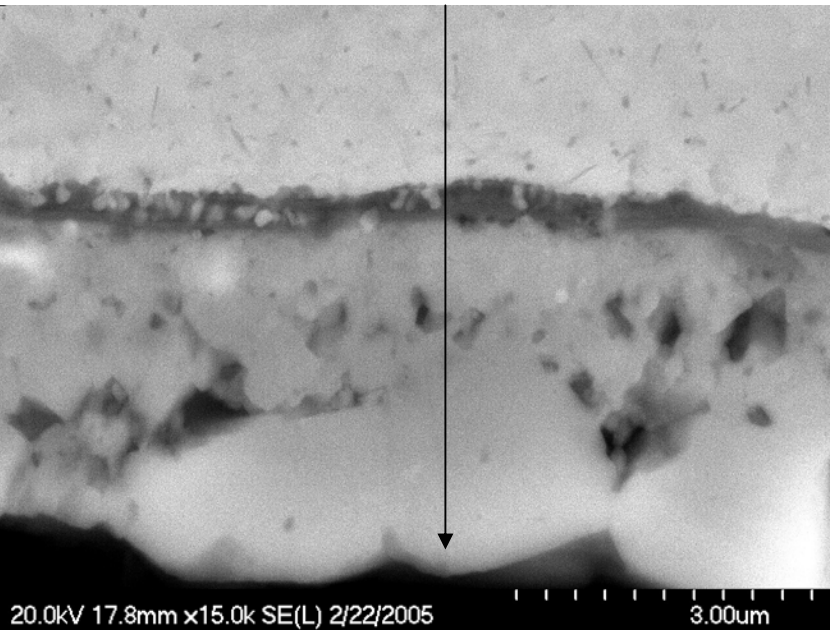


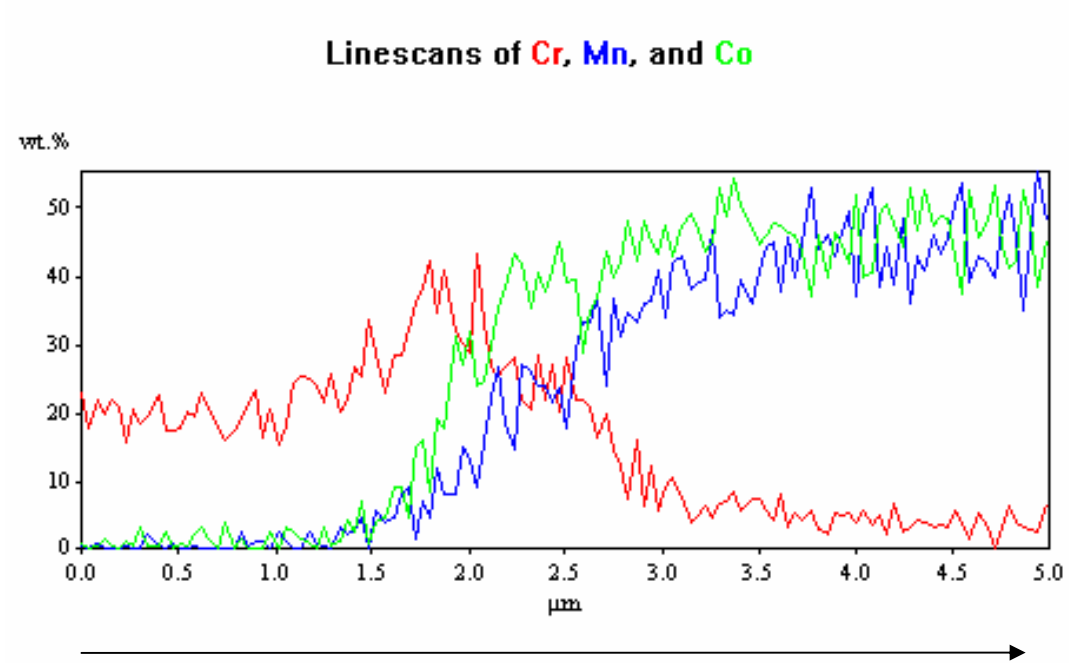
As deposited, amorphous or ultrafine polycrystalline CrON/AlON + $(Co,Mn)_3O_4$ dual segment coating



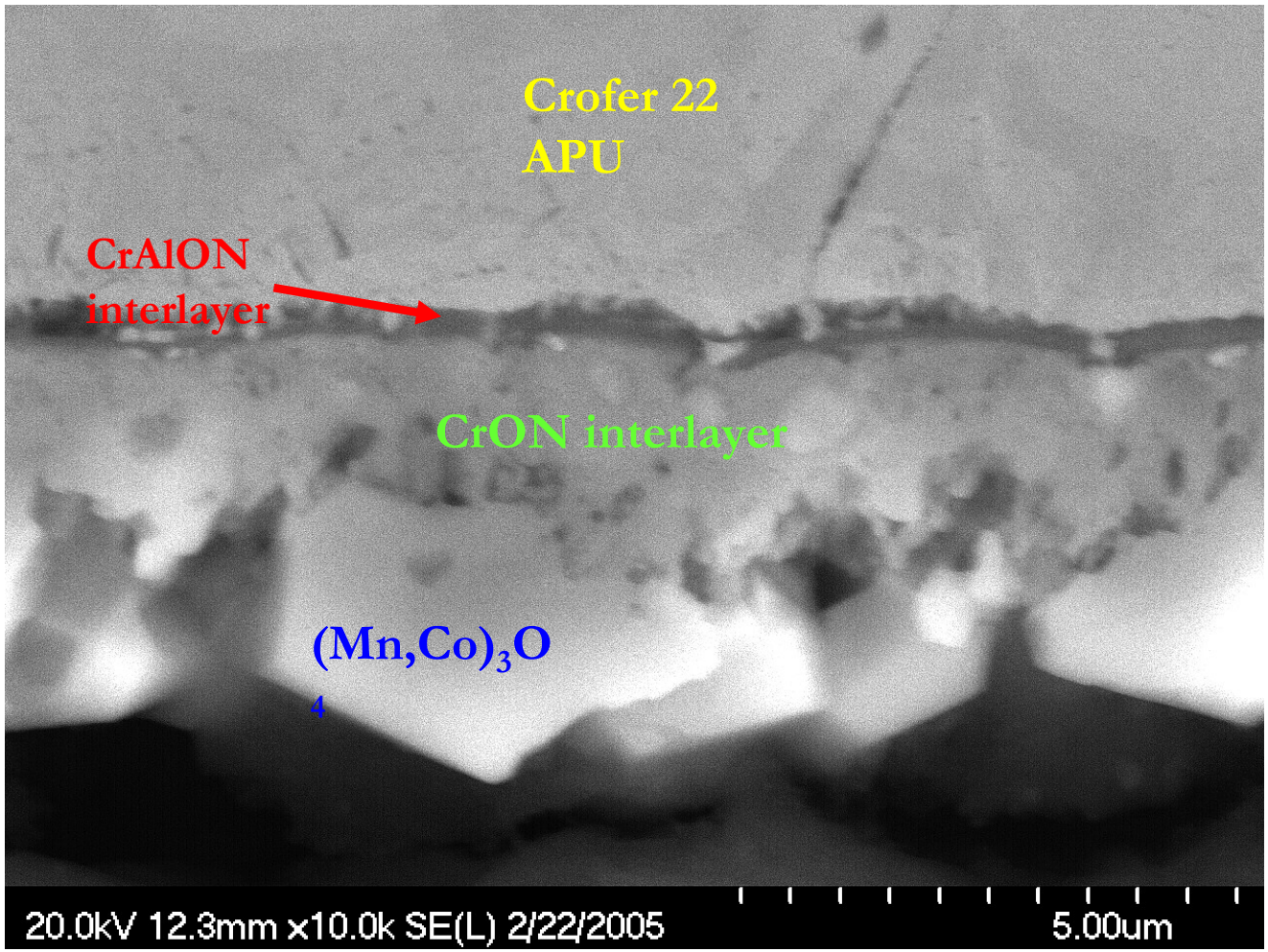
Post 2000+ hrs oxidation, 800C in air, polycrystalline CrON/AlON + $(Co,Mn)_3O_4$ dual segment coating

CrON/AlON+$(Co,Mn)_3O_4$ Dual Segment Coating Cross-Section: Post 2000+ hrs oxidation at 800C in air

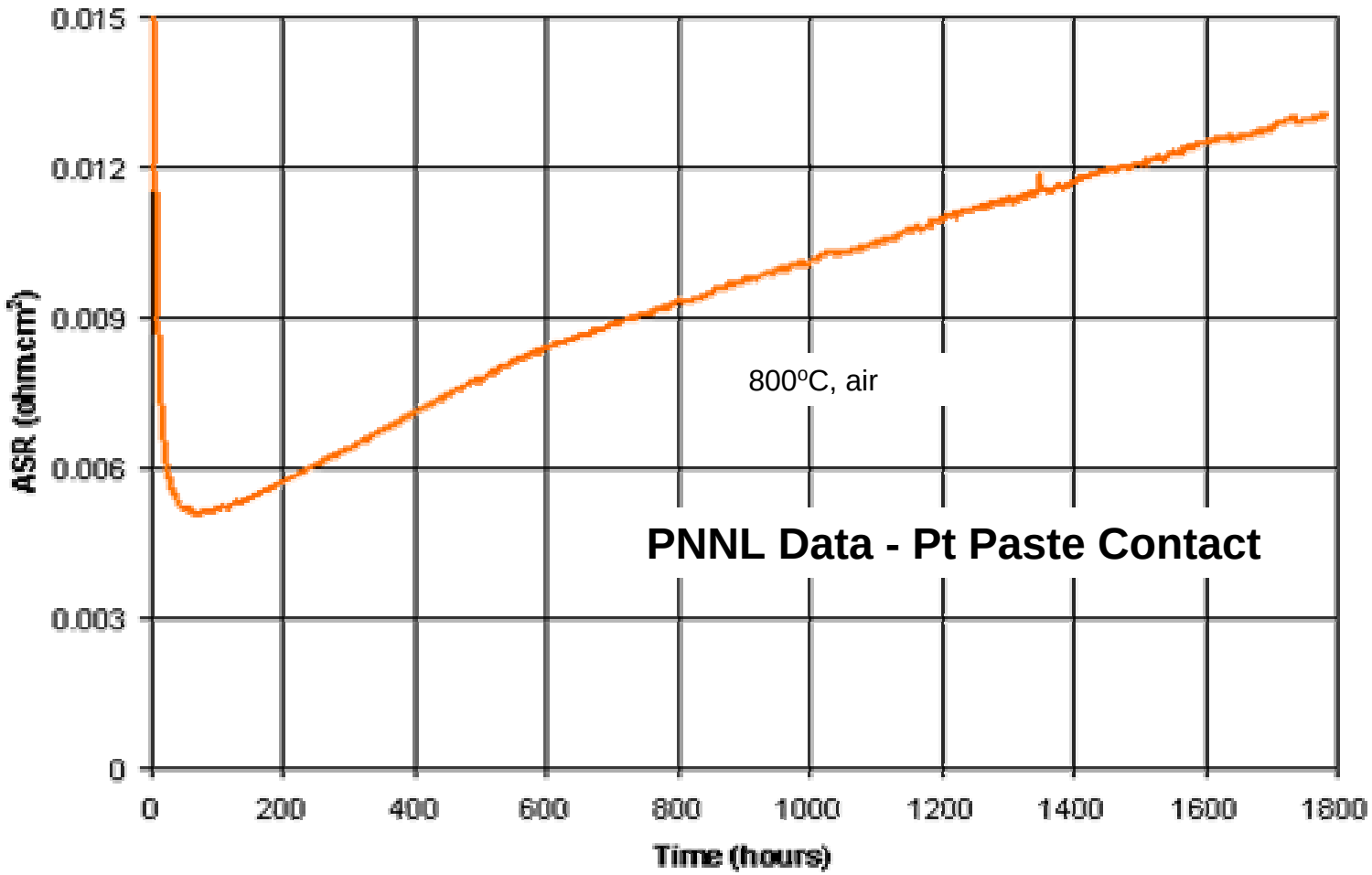




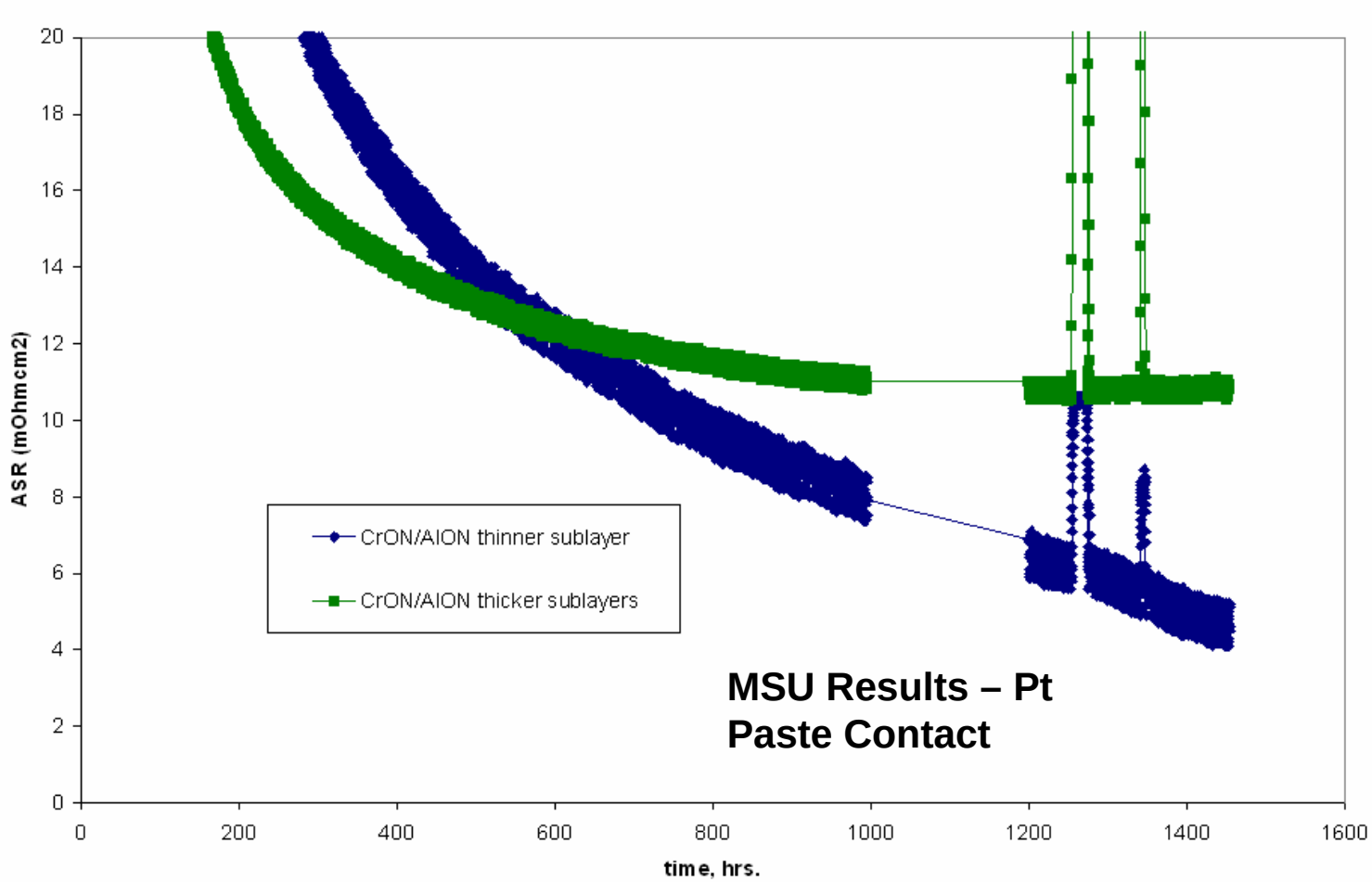
CrON/AlON+$(Co,Mn)_3O_4$ Dual Segment Coating Cross-Section: Post 2000+ hrs oxidation at 800C in air (Cont.)



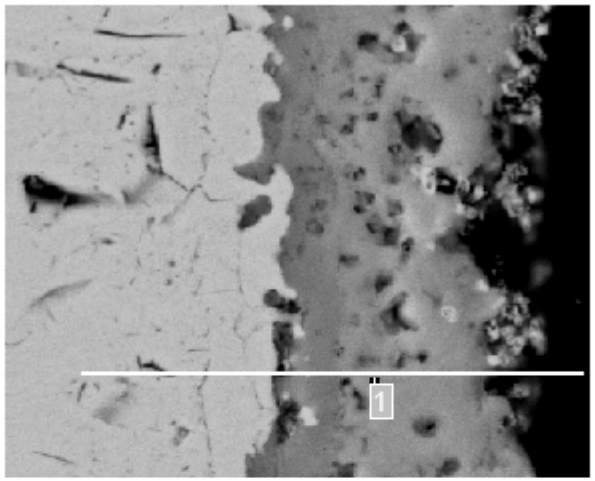
ASR of uncoated Crofer 22 APU

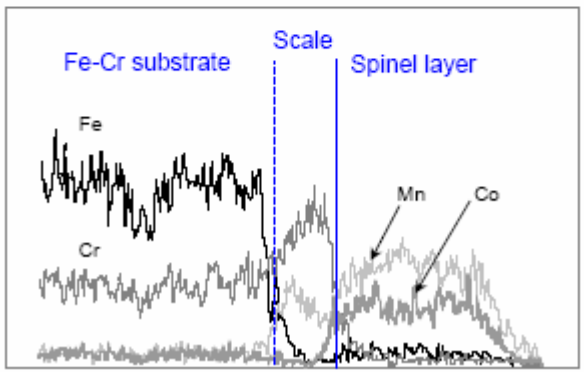


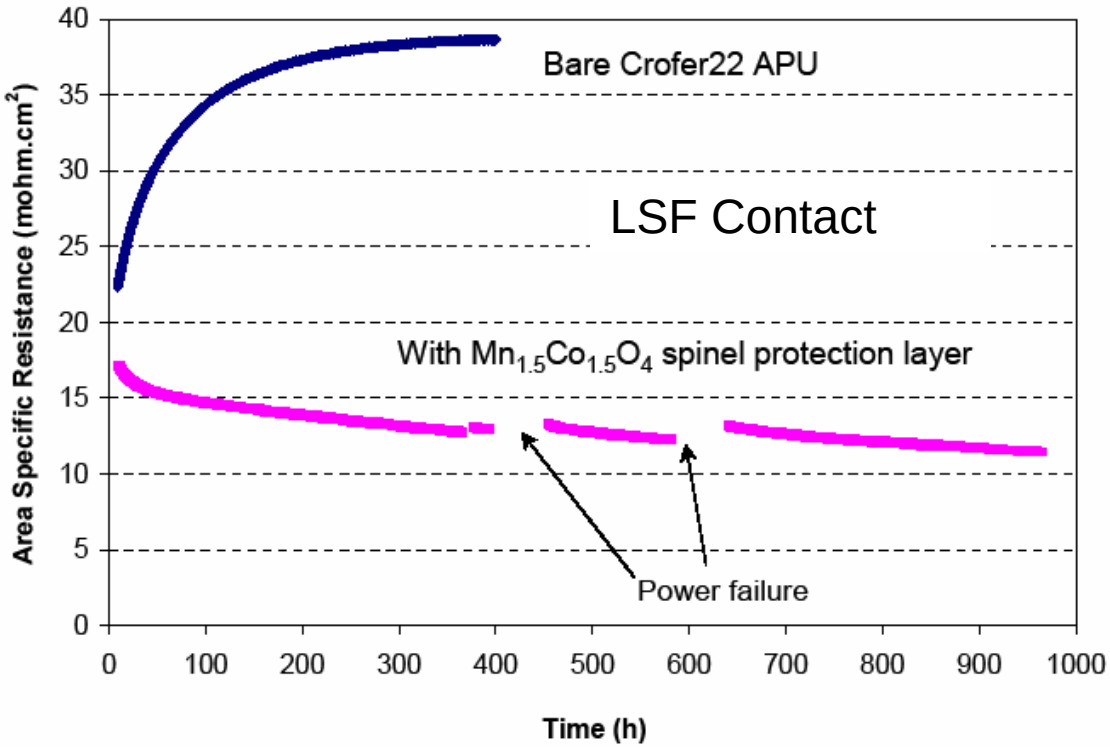
ASR of Filtered Arc CrON/AlON bond segment coating on Crofer 22 APU



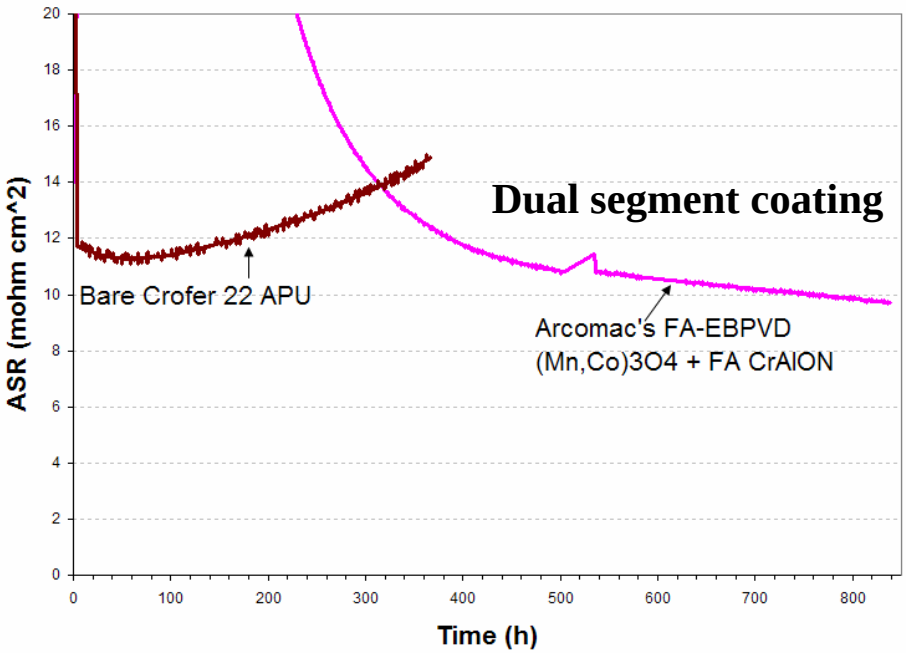
PNNL Screen Printed $(Mn,Co)_3O_4$ Coating Results

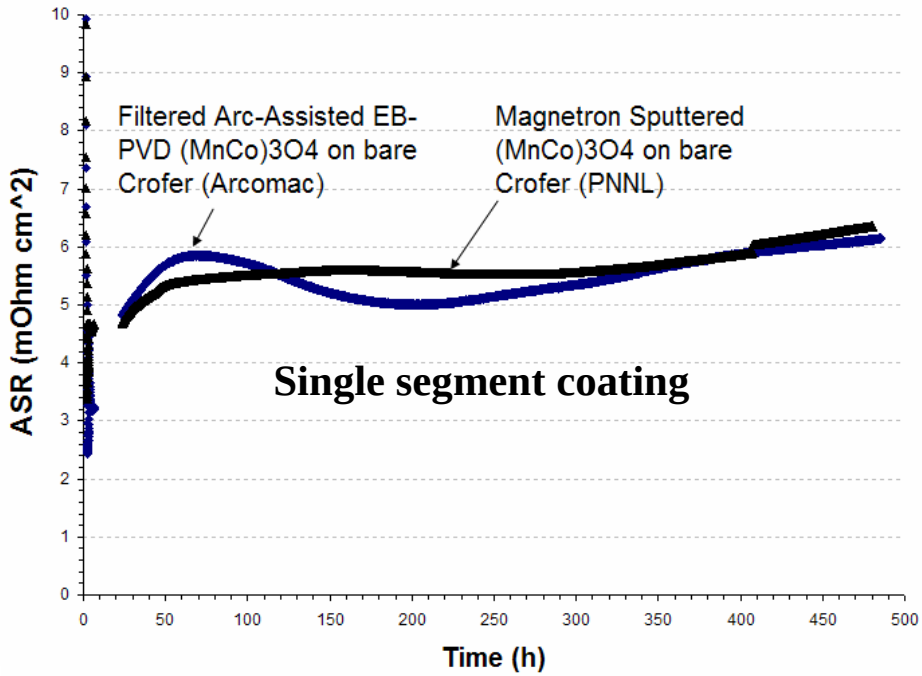






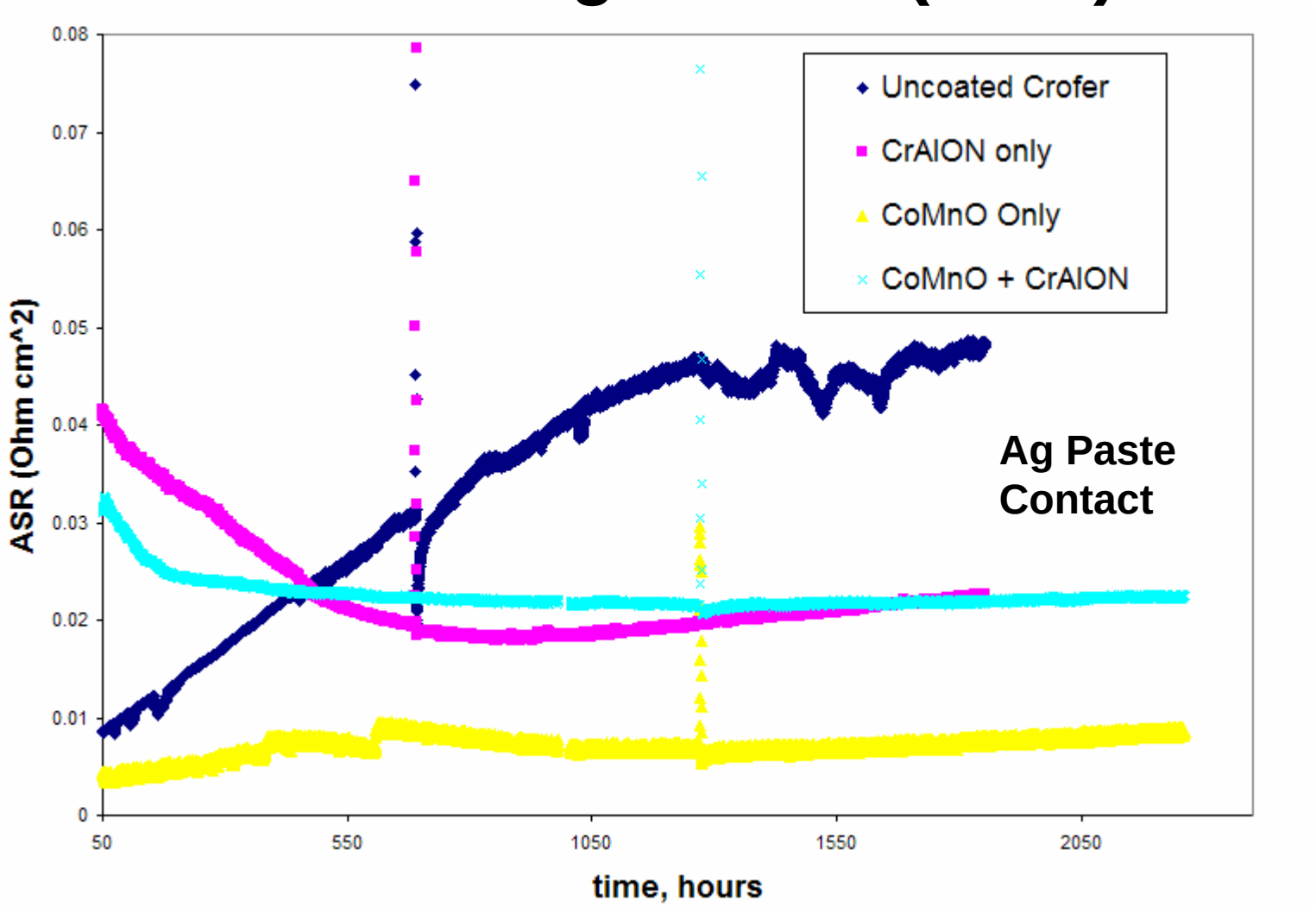
PNNL testing results : ASR of Crofer 22 APU coated by various PVD coating techniques





(Ag paste contact)

ASR testing results (MSU)



Summary

- **Hybrid Filtered Arc/EBPVD process is highly productive and cost effective way to fabricate protection coatings for metallic IC**
- **PVD coating provides high uniformity over large coating areas**
- **Two-segment CrAlON + (Mn,Co)3O4 coating provides excellent adhesion, HT spallation resistance and serves as a barrier against oxygen inward and chromium outward diffusion, blocking growth of TGO and preventing chromium migration onto the surface**

Future Works

- **Optimizing the hybrid FA/EBPVD process to better control coating structure and morphology. This includes both coating composition and architecture optimization**
- **Evaluate long term stability under SOFC operating conditions**
- **Investigate and optimize the thermal cycling performance**
- **The capability for mass production of the coatings will be demonstrated to meet performance and cost targets using newly manufactured 200 kW evaporation power FA/EBPVD surface engineering system at Arcomac**

Acknowledgements

- DoE/NETL: Travis Shultz and Lane Wilson
- DoE/PNNL: Gary McVay and Larry Pederson
- MSU/HiTEC: Lee Spangler