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

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

This Program is Supported by DoE/SECA Contract
No. DE-FC26-04NT42225
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- 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/AION (oxidation resistant diffusion barrier, bond coating)
  - 2nd Segment – columnar grain (Mn,Co)₂O₄ (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)₂O₄ Columnar FAD assisted EBPVD deposit – electrically conductive and accommodates cathode/interconnect interfacial stresses
- CoCrAION nanolaminated FAD corrosion resistant bond interlayer – improves coating adhesion and blocks O₂ 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 ~1μm/hr
- Filtered Arc-Assisted FA/EBPVD (Mn,Co)3O4 ~6μm/hr @ 300W EB Power
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
Oxidation kinetics of St.St. with Filtered Arc CrAlN coatings of various architectures

Sample 026: 0 hrs

Sample 026: 4 hrs

Sample 026: 0 hrs

Sample 026: 4 hrs

Sample 026: 0 hrs

Sample 026: 4 hrs

RBS Concentration Profiles: Before (top) after (bottom) 4 hrs @ 800 C in air
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 ~3-5µm
~750 hrs @800°C

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

Coated Crofer 22APU
Scale/Coating ~1µm
1000+ hrs @800°C
Coating Adhesion Assessment - Rockwell 145kg Indentations

2-Segment Coating
Lower, nanolaminated CrCoON/AION Bond-Coat with Upper (Mn,Co)₃O₄
(Excellent Adhesion)

1-Segment Coating
Upper (Mn,Co)₃O₄ Only
(Fair Adhesion)
(Co,Mn)$_3$O$_4$ Single Segment Coating Recrystallization

As deposited, amorphous or ultrafine polycrystalline (Co,Mn)$_3$O$_4$ single layer coating

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

Post 2000+ hrs oxidation, 800C in air, polycrystalline (Co,Mn)$_3$O$_4$ single layer coating
CrON/AlON+(Co,Mn)$_3$O$_4$ Dual Segment Coating Recrystallization

As deposited, amorphous or ultrafine polycrystalline CrON/AlON + (Co,Mn)$_3$O$_4$ dual segment coating

Post 2000+ hrs oxidation, 800C in air, polycrystalline CrON/AlON + (Co,Mn)$_3$O$_4$ dual segment coating
CrON/AION+(Co,Mn)$_3$O$_4$ Dual Segment Coating Cross-Section:
Post 2000+ hrs oxidation at 800C in air
CrON/AION+(Co,Mn)$_3$O$_4$ Dual Segment Coating Cross-Section:
Post 2000+ hrs oxidation at 800°C in air (Cont.)
ASR of uncoated Crofer 22 APU

800°C, air

PNNL Data - Pt Paste Contact
ASR of Filtered Arc CrON/AION bond segment coating on Crofer 22 APU

MSU Results – Pt Paste Contact
PNNL Screen Printed (Mn,Co)$_3$O$_4$ Coating Results

![Image of electron microscope image showing Fe-Cr substrate, scale, and spinel layer with Fe, Cr, Mn, and Co peaks]

![Graph showing area specific resistance (mohm/cm$^2$) over time (h) for Bare Crofer22 APU, LSF Contact, and With Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel protection layer, with marked points for power failure.]
PNNL testing results: ASR of Crofer 22 APU coated by various PVD coating techniques

Dual segment coating

Single segment coating

(Ag paste contact)
ASR testing results (MSU)

- Uncoated Crofer
- CrAlON only
- CoMnO Only
- CoMnO + CrAlON

Ag Paste Contact

Graph showing ASR (Ohm cm^2) over time (hours) for different coatings.
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