IV.A.2 Oxidation Resistant, Cr Retaining, Electrically Conductive Coatings on Metallic Alloys for SOFC Interconnects

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Objectives

- Enable the use of inexpensive ferritic stainless steels (FSSs) as planar solid oxide fuel cell (SOFC) interconnects (ICs) via advanced physical vapor deposition protective coatings.
- Develop and demonstrate novel, cost-effective coating deposition processes to establish dense and uniform protective and functional coatings on FSS SOFC-IC substrates.
- Evaluate protective coatings during SOFC-IC relevant exposures.
- Optimize coating deposition process parameters to maximize SOFC-IC performance and ultimately reduce cost.

Accomplishments

- Developed and tested novel, hybrid surface engineering technologies combing large area filtered arc deposition (LAFAD), electron beam physical vapor deposition (EBPVD), unbalanced magnetron (UBM) and thermal evaporation to deposit dense, protective coatings in an economical manner.
- Engineered LAFAD coatings to combine favorable electronic conductivity and transport barrier characteristics. Diffusion-barrier amorphous Al and Cr oxide coatings were embedded with electronically conductive Co and/or Mn-containing spinel oxide crystallites.
- Achieved low, stable area specific resistance (ASR) of <50 Ohm•cm^2 for >1,000 hours in 800°C air in contact with porous lanthanum strontium manganate (LSM).
- Significantly reduced Cr volatility. 430 FSS with ~2 µm LAFAD nanocomposite TiCrAlY oxide coating exhibited negligible Cr volatility compared with uncoated counterparts, in spite of the coating containing ~12 at% Cr.
- Demonstrated protective, stable amorphous coatings for sealing areas with high ASR values and negligible chemical or physical changes after >1,000 hours in 800°C air.
- Developed thermochemical modeling of multi-elemental high temperature oxicermet coatings.

Introduction

To achieve Solid State Energy Conversion Alliance (SECA) cost and performance goals, attention has been directed toward inexpensive FSSs as SOFC-ICs. Currently, the SOFC-IC in planar SOFC systems accounts for a dominant portion of the overall stack cost. Inexpensive FSSs meet many SOFC-IC functional requirements; however, during operation, FSSs form blanketing thermally-grown chromium oxide (TGO) scales, which dramatically degrade SOFC stack performance and limit device life-time. To date, deleterious issues with Cr volatility, electrical resistance and thermal-chemical incompatibilities with adjoining components have restricted the use of FSSs as SOFC-ICs. Since 2004, Arcomac Surface Engineering, LLC (ASE) has been engaged in the development of protective and functional coatings on FSSs as SOFC-ICs. ASE has developed advanced coating deposition technologies, which show promise for resolving both SOFC-IC performance requirements in an economically-feasible manner.

Approach

ASE is developing hybrid, filtered arc plasma deposition technologies to establish protective, functional coatings on commercially available FSSs. Coating design is aimed at inhibiting ionic transport and Cr volatility, while retaining low and stable ASR at ~800ºC in air during long-term exposures. Desired coating compositions and architectures are determined through thermodynamic and transport modeling in addition to prior art. Appropriate deposition materials are acquired and deposition processes are designed and performed using ASE patented equipment and technologies. Coated samples are exposed to conditions simulating SOFC-IC operation, and complimentary surface analyses are conducted to evaluate performance. Results are employed to assist in developing new coating deposition process formulations. Promising coating systems from preliminary testing are then subjected to more prototypical SOFC interconnect conditions

for further assessments. Concurrently, economic evaluations of coating process and SOFC-IC fabrication are ongoing.

Results

The patented filtered arc plasma source ion deposition (FAPSID) system developed by ASE utilizes two dual filtered cathodic arc LAFAD sources in conjunction with two UBM sputtering sources, two EBPVD evaporators and a thermal resistance evaporation source in one, universal vacuum chamber layout (as illustrated in Figure 1) [1-4]. This system has demonstrated the capability to deposit nanocomposite, nanolayered coatings with a wide-variety of compositions and architectures. Photographs of uncoated and LAFAD coated (~2 µm TiCoMnCrAlYO) FSS sheets of typical SOFC-IC geometry are shown in Figure 2. The FSS sheets show laser cut specimen tabs used for specific SOFC-IC testing.

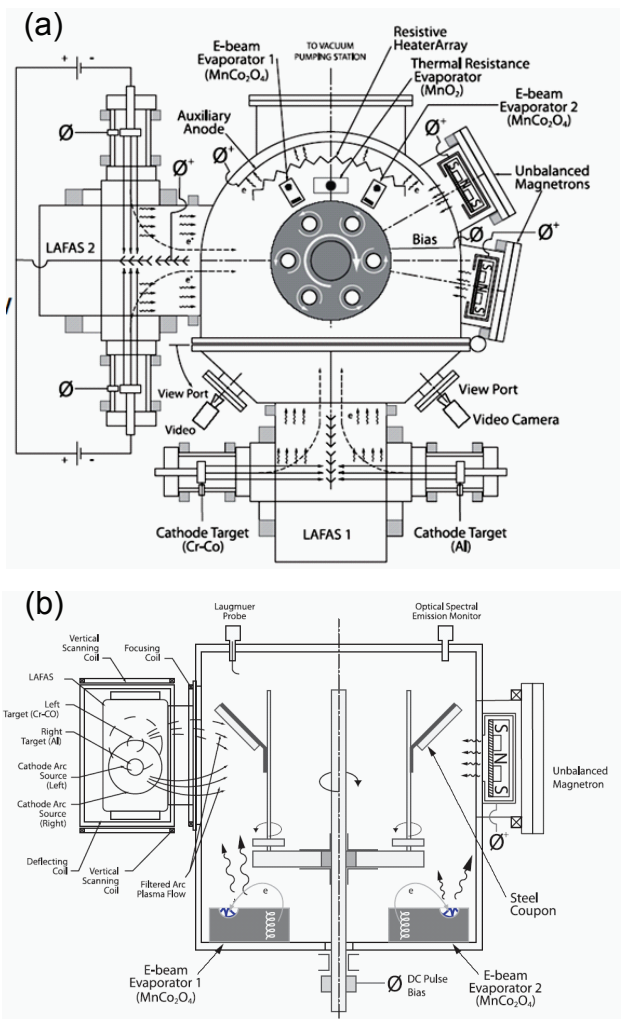

FIGURE 1. Schematic Illustration of the FAPSID Surface Engineering System, Showing (a) Top View; and (b) Side View

The most promising ASE coatings yet identified are LAFAD nanostructured coatings from the MCrAlYO system (where M = Co, Ti, and/or Mn). These coatings are designed to function as effective barriers, blocking both inward and outward ionic diffusion, while providing adequate electronic conductivity through the coating thickness. The transition metal dopants are selected to increase high-temperature electronic conductivity by forming nanocomposite thermistor-like oxicermets. Thermochemical modeling, using the advanced "TERRA" thermodynamic equilibrium calculation code with solid solution considerations, is being used to estimate phase composition of multielemental oxicermet coatings and their interactions with SOFC-IC operating environments. An extensive matrix of LAFAD coatings have been successfully deposited with excellent adhesion to various FSS substrates under consideration for SOFC-ICs. Other hybrid coating deposition methods, employing filtered arc assisted thermal resistance evaporation and filtered arc assisted electron beam evaporation are also being explored.

SOFC IC-relevant behavior of coated and uncoated samples, i.e. high temperature oxidation, ASR, and Cr volatility have been investigated in collaboration with researchers at Montana State University, Pacific Northwest National Laboratory (PNNL), Lawrence Berkeley National Laboratory (LBNL) and NASA-Glenn Research Center. Summary ASR data from FSS uncoated and with four different LAFAD coatings is shown in Figure 3. The ASR of the uncoated FSS continues to increase due to the growth of the chromia-based TGO scale. The ASR of the coated specimens generally decreases and stabilizes. The decrease is attributed to the restructuring of the as-deposited amorphous coating into a polycrystalline film. The stability is attributed to the transport-barrier properties of the coatings, whose thicknesses and chemical composition do not change appreciably during the 1,000 hour ASR test. LAFAD coatings with Co and/or

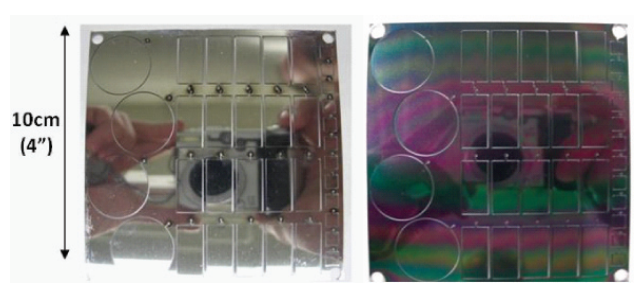

FIGURE 2. Photographs of Uncoated (left) and Coated (right) FSS Sheets (100 x 100 x 1 mm) with Laser Cut Specimen Tabs of Various Testing Geometries

Mn exhibit significantly lower initial ASR than those without. The TiCrAlYO and CrAlYO coatings are permeable to the high-oxygen-affinity Mn from the FSS, and evolve percolating networks of conductive Mn-containing oxides, thus lowering the ASR over time.

Figure 4 displays a summary of Cr volatility results from uncoated and LAFAD TiCrAlYO coated FSS. The graph displays the cumulative amount of Cr collected during the test. The uncoated FSS continues to volatilize Cr throughout the test, while the coated specimen demonstrates negligible Cr volatility after the first 24 hours. This coating contains ~12 at% Cr; however, the Cr is apparently sequestered in a solid solution with complex Al-containing oxides, which agrees well with thermochemical modeling.

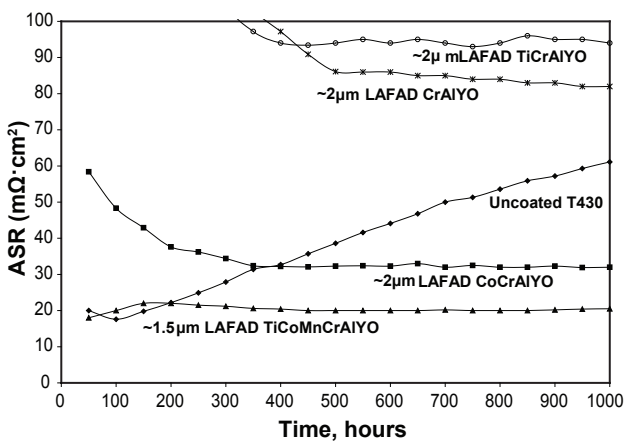

FIGURE 3. Summary ASR Data for Uncoated and Three Different LAFAD MCrAlYO Coated FSS

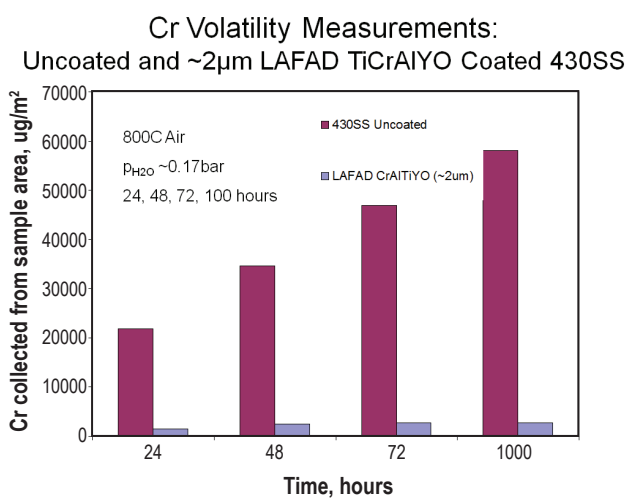

FIGURE 4. Cumulative, Time-Dependant Cr Volatility Data for Uncoated and TiCrAlYO Coated FSS

Conclusions and Future Directions

ASE has developed advanced coating deposition processes, which may enable the use of inexpensive metallic alloys as interconnect components in planar SOFC systems. Nanostructured oxicermet coatings, deposited by hybrid filtered arc assisted techniques are being investigated to meet SECA SOFC-IC performance and cost requirements. A large-scale FAPSID surface engineering process, offering favorable economics through high yield and advanced hybrid design, is under investigation for deposition of protective coatings on SOFC-ICs. Based upon success with similar physical vapor deposition (PVD) processes, cost estimates for this process at full-scale production reach ~$0.10 per SOFC-IC. Future work will focus on cross comparison with other coatings on identical FSS samples and testing in short SOFC stacks. Coating composition and architecture will be continually optimized to further improve thermal-chemical and mechanical stability, transport barrier properties and low ASR during long-term operation.

FY 2007 Publications/Presentations

1. "Deposition and evaluation of protective PVD coatings on ferritic stainless-steel SOFC interconnects" V.I. Gorokhovsky, P.E. Gannon, M.C. Deibert, R.J. Smith, A. Kayani, M. Kopczyk, D. VanVorous, Zhenguo Yang, J.W. Stevenson, S. Visco, C. Jacobson, H. Kurokawa, and S.W. Sofie, *Journal of Electrochemical Society* 153 (10) A1886-A1893 2006.

2. "Enabling inexpensive alloys as SOFC interconnects: an investigation into hybrid coating technologies to deposit nanocomposite functional coatings on ferritic stainless steels" P.E. Gannon, V.I. Gorokhovsky, M.C. Deibert, R.J. Smith, A. Kayani, P.T. White, Z. Gary Yang, D. McCready, S. Visco, C. Jacobson, and H. Kurokawa, *International Journal of Hydrogen Energy* In-press.

3. "Oxidation resistance of magnetron-sputtered CrAlN coatings on 430 steel at 800°C" A. Kayani, T.L. Buchanan, M. Kopczyk, C. Collins, J. Lucas, K. Lund, R. Hutchison, P.E. Gannon, M.C. Deibert, R.J. Smith, D.-S. Choi, and V.I. Gorokhovsky, *Surface and Coatings Technology* 201, n. 7 SPEC. ISS., December 20, 2006, p. 4460–4466.

4. "Chromium volatility of coated and uncoated steel interconnects for SOFCs" C. Collins, J. Lucas, T.L. Buchanan, M. Kopczyk, A. Kayani, P.E. Gannon, M.C. Deibert, R.J. Smith, D.-S. Choi, and V.I. Gorokhovsky, *Surface and Coatings Technology*, v. 201, n. 7 SPEC. ISS., December 20, 2006, p. 4467–4470.

5. "Oxidation studies of CrAlON nanolayered coatings on steel plates" A. Kayani, R.J. Smith, S. Teintze, M. Kopczyk, P.E. Gannon, M.C. Deibert, V.I. Gorokhovsky,

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6. "Overview of current trends in SOFC materials" in New Developments in Advanced Functional Ceramics Massimo Viviani, Paolo Piccardo, Antonio Barbucci, Daria Vladikova, Zdravko Stoynov, Vladimir Gorokhovsky and Paul Gannon, 2007: ISBN: 81-7895-248-3 Editor: Liliana Mitoseriu.

7. "Advanced PVD Nanocomposite Protective Coatings for SOFC Metallic Interconnects" Invited Presentation - TMS Annual Meeting; February 25 – March 1, 2007; Orlando, FL.

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2. V.Gorokhovsky, US Pat. Application No. 20040168637A1.

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