A Metallic Interconnect for Intermediate Temperature Planar, Solid Oxide Fuel Cells (SOFC)

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Objectives

- Develop coatings for metallic interconnects
- Outline a methodology for selecting interconnect materials
  - Alloys and coatings
- Develop oxidation kinetics models for coatings
- Deposit coatings on metallic interconnects
  - Electron beam vaporization
  - Sputtering
  - Solution techniques
- Evaluate Coatings
  - Phase assemblage
  - Electrical conductivity
  - Oxidation kinetics
- Test Interconnects in Planar SOFC stacks

Two Coating Approaches

Protective Coating

- Desired oxide coating deposited directly on interconnect
- Decrease oxidation rate
- Increase electronic conductivity
- Suppress chromium evaporation

Consumptive Coating

- Coating reacts with naturally occurring oxide (Cr_2O_3)
- Resulting phase exhibits better electronic conductivity
- Resulting phase suppresses oxidation kinetics
- Resulting phase suppresses volatilization of chromium

Deposition of Coatings

Protective Coatings

- Directly deposit desired coating
- Perovskites: Sr doped $LaMnO_3$, Sr doped $LaCoO_3$, Sr doped $LaCrO_3$
- Spinels: $Mn_{2-x}Cr_{1+x}O_4$ $(0 \le x \le 1)$

Consumptive Coatings

Metals deposited

Mn, Co, Cr, In, Fe, Zn	Spinel Formers	A_2BO_4
La	Perovskite Former	ABO_3

Co-deposition

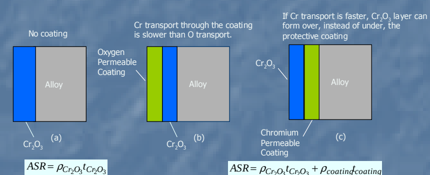
Mn and Co	$(Mn, Co)_3O_4$
La, Sr, Mn	LSM Perovskite

Deposition techniques
- Electron Beam Vapor Deposition
- Spray coating
- Dip coating
- Spin coating
- Electroplating

Two-Probe Resistance Measurement

Resistance measurements:
Temperatures: 200 to 800 °C
Atmospheres: Air and Hydrogen, Dry and Wet

Schematic Showing Oxide Formation on Coated and Uncoated Cr-based Alloys



$ASR = \rho_{Cr_2O_3} t_{Cr_2O_3}$ $\quad$ $ASR = \rho_{Cr_2O_3} t_{Cr_2O_3} + \rho_{coating} t_{coating}$

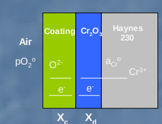
The coating should be such that ASR(coating) < ASR(Cr_2O_3)

Required properties of the coating: (1) Should not readily transport oxygen.
(2) Should be a good electronic conductor.

Possible coatings: (1) Perovskites (ABO_3). (2) Spinels (AB_2O_4).

Oxidation Model

$$X_d^2 + \frac{9\tilde{D}_{Cr} C_{Cr} X_c}{2\tilde{D}_O C_O} X_d = \frac{3V_C \tilde{D}_{Cr} C_{Cr}}{4N_A}\left[\frac{4}{3}\ln a_{Cr}^o - \frac{2}{3}\frac{\Delta G^o}{RT} - \ln p_{O_2}^o\right] t$$



X_d = Thickness of oxide layer (Cr_2O_3) formed at time 't'
X_C = Thickness of deposited coating
$\tilde{D}_O$ = Chemical diffusion coefficient of O in the deposited coating
C_O = Concentration of O in the deposited LSM coating
$\tilde{D}_{Cr}$ = Chemical diffusion coefficent of Cr in the oxide formed (Cr_2O_3)
C_{Cr} = Concentration of Cr in the oxide formed (Cr_2O_3)
V_d = Molar volume of the formed oxide layer, Cr_2O_3
N_A = Advogadro's number
a_{Cr}^o = Activity of Cr at the alloy-chromite interface
ΔG^o = Standard free energy of $2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3$
$p_{O_2}^o$ = Partial pressure of O_2 at the coating-atmosphere interface

Limiting Case (I):

$$X_d \approx \frac{\tilde{D}_O C_O V_d}{6N_A X_C}\left[\frac{4}{3}\ln a_{Cr}^o - \frac{2}{3}\frac{\Delta G^o}{RT} - \ln p_{O_2}^o\right] t$$

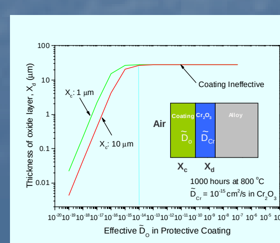
Oxidation kinetics are linear, similar to interface-controlled
Oxidation rate determined by oxide ion diffusivity in coating

Limiting Case (II):

$$X_d \approx \sqrt{\frac{3V_d \tilde{D}_{Cr} C_{Cr}}{4N_A}\left[\frac{4}{3}\ln a_{Cr}^o - \frac{2}{3}\frac{\Delta G^o}{RT} - \ln p_{O_2}^o\right]}\sqrt{t}$$

Oxidation kinetics are parabolic, similar to diffusion-controlled
Oxidation rate dictated by Cr diffusivity in formed oxide layer

Illustrative Calculation of Coating Effectiveness

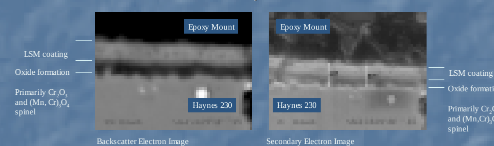


Deposition of oxide coatings by sputtering

Substrate is 5 mil Haynes 230
- Ni, Cr superalloy
- 56% Ni, 26% Cr, 0.75% Mn, 5.3% Co, 4.8% W, Fe, Mo,
- Oxide Layer Formation: Cr_2O_3, $(Mn, Cr)_3O_4$ spinel

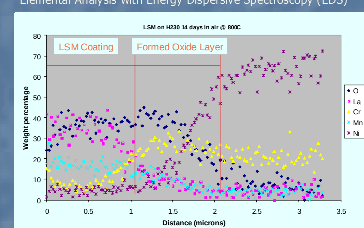
Oxide layers deposited by sputtering
- RF, 200 W, Argon
- $La_{0.85}Sr_{0.15}MnO_{3-\delta}$ Perovskite Phase
- Mn_2CrO_4 Spinel Phase
- Thickness of 1.3 μm

Sputtered LSM coating on Haynes 230 Oxidized for 14 days at 800 °C in air

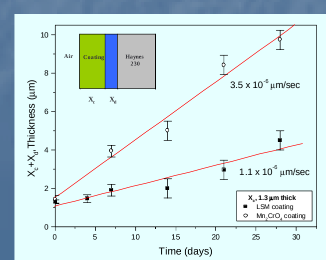


Sputtered LSM coating on Haynes 230 Oxidized for 14 days at 800 °C in air

Elemental Analysis with Energy Dispersive Spectroscopy (EDS)



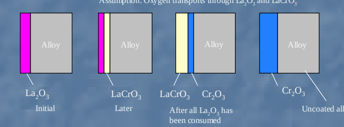
Thickness of $X_c + X_d$ on LSM and Mn_2CrO_4 coated Haynes 230 oxidized in air @ 800 °C



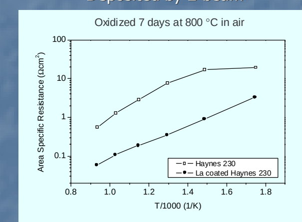
Consumptive Coating

Schematic of Oxidation Progression on La_2O_3 Coated Alloy

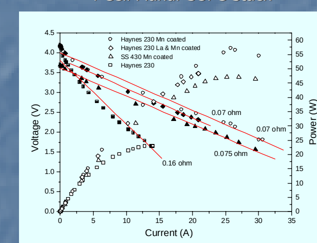
Assumption: Oxygen transports through La_2O_3 and $LaCrO_3$



La coated Haynes 230 Deposited by E-beam



4-Cell Planar SOFC Stack



Summary

- Developed oxidation models for both protective and consumptive coatings
- Two limiting cases of oxidation:
  1) linear (coating limited)
  2) parabolic (diffusion limited by oxide formation on alloy)
- Deposited protective coatings on metallic interconnects
  - Perovskites and Mn-based Spinels
- Oxidation kinetics exhibits linear behavior and is dictated by oxide ion diffusivity in the protective coating
- Consumptive coatings produced by depositing metals including Mn, Co, and La
- Consumptive coatings promote the formation of Spinel and Perovskite phases that exhibit higher electronic conductivity than the native oxide
- The area specific resistance of oxidized Ni-Cr alloys was reduced by over an order of magnitude with coatings
- The reduced ASR of the interconnects resulted in a doubling of the power density of the planar SOFC stacks

Acknowledgements

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