Anomalous Oxidation of Ferritic Stainless Steels under Air//Hydrogen Fuel Dual Environments

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Solid Oxide Fuel Cell Operation

Electrochemical and Reformation Processes

**Fuel:** CH₄, H₂, CO, CO₂, H₂O

**Anodic Reaction**
Electrochemical Oxidation:
- H₂+O²⁻ = H₂O + 2e
- CO+O²⁻ = CO² + 2e

Steam reforming:
- CH₄+H₂O = CO+ 3H₂

Shift Reaction:
- CO+H₂O = CO₂+ H₂

**Cathodic Reaction**
Oxidant: Air, O₂

- 1/2O₂ + 2e = O²⁻

**Overall Cell Reaction**
- H₂+1/2O₂ = H₂O
- CO+1/2O₂ = CO₂
Planar Solid Oxide Fuel Cells

Repeat Components

Oxidation resistance alloy interconnects have been used in planar SOFC systems
Interconnect: Functions & Exposure Conditions

Functions

1) Acts as physical barrier, hermetically separating fuel and oxidant.
2) Acts as a low resistant electrical conduit over life time of the device.
3) Provides mechanical support and stability to the stacks.

Exposure conditions

1. Simultaneously exposed to oxidizing gas at anode side and fuel gas at anode side.
2. Compliant seal/metal interface.
3. Electrical contact/metal interface.
4. Ambient/metal interface.

Cells

H₂, CO, H₂O, CO₂, etc.

Air or O₂, H₂O.
Overall, heat resistant alloys could be potential candidates, including:

- Ferritic stainless steels
- Austenitic stainless steels
- Fe-Ni-base superalloys
- Ni-Fe-base superalloys
- Cr-base alloys

Plus

- Co-base superalloys

Ferritic stainless steels offer a combination of good CTE matching and manufacturability, as well as being cost-effective.
Motivation

- Oxidation has been a common area of interest and widely studied in the past century.
- But the studies were typically carried out in a single exposure.
- The oxidation behavior under “simultaneous” dual exposures is indeed unclear.
- Understanding helps develop robust materials and improve reliability and durability of components such as interconnects that function under dual exposures.
Interconnect “Dual” Exposures

Hydrogen

Metal substrate

Air or moist air

Reformate

Metal substrate

Air or moist air

H₂//Air

Reformate//Air
Oxidation Study under H₂//Air Dual Exposures

Variables:
- Alloy composition
  - E-brite-27%Cr
  - Crofer22-22%Cr
  - AISI430-17%Cr
- Water vapor effects
- Thermal history: isothermal vs. cycling
Crofer22 APU: Scale Growth in Air Only

Crofer22 APU is characterized by formation of a unique scale that is comprised of course, column-grown (Mn,Cr)$_3$O$_4$ toper layer and a fine, granular Cr$_2$O$_3$-rich sub-layer.

**In-situ X-Ray Diffraction Analysis**

M: Fe-Cr substrate  
C: Cr$_2$O$_3$  
S: (Mn,Cr)$_3$O$_4$ spinel

![X-Ray Diffraction Peaks](image-url)
Grown on the coupon in air only and at the airside of the coupon that was **ISOTHERMALLY** heat-treated at 800°C, 300 hours.

*M = Fe-Cr Substrate;  
C = Cr$_2$O$_3$;  
S = M$_3$O$_4$ (M=Mn, Cr, and/or Fe)*
Crofer22 APU: Scale Microstructures

Air exposure at both sides

Surface microstructures

Air-side of dual test

Cross-sections

(Mn,Cr)₃O₄ + Cr₂O₃

Fe

Cr

Mn

(Mn,Fe)₃O₄ + Cr₂O₃

Fe

Cr

Mn
Scale Growth on Airside

Fe enrichment found both in (Mn,Cr,Fe)$_3$O$_4$ grains and at grain boundaries.
Crofer22 APU (22%Cr): Structure of Scales

Grown on the coupon in fuel (H₂ + 3%H₂O) only and at the fuel side of the coupon that was **ISOTHERMALLY** heat-treated at 800°C, 300 hours.

M = Fe-Cr Substrate;  
C = Cr₂O₃;  
S = M₃O₄ (M=Mn, Cr)

(97%H₂/3%H₂O) side of dual exposures

Both sides exposed to (97%H₂/3%H₂O)
Crofer22 APU: Scale Microstructures

Surface microstructures

Fuel exposure at both sides

Fuel side of dual test

Cross-sections

(Mn,Cr)\textsubscript{3}O\textsubscript{4} + Cr\textsubscript{2}O\textsubscript{3}

(Mn,Cr)\textsubscript{3}O\textsubscript{4} + Cr\textsubscript{2}O\textsubscript{3}
Effects of Water Vapor

Ambient air was replaced by moist air, increasing water content from 1% to 3%.
Crofer 22 APU: Effects of Water Vapor

Grown on the Crofer 22 APU coupon in air (3% H₂O) only and at the airside of the coupon that was heat-treated at 800°C, three cycles with each cycle of 100 hours.

\[ M = \text{Fe-Cr Substrate}; \quad C = \text{Cr}_2\text{O}_3 \]
\[ S = \text{M}_3\text{O}_4 (M=\text{Mn, Cr, and/or Fe}); \quad H = \alpha-\text{Fe}_2\text{O}_3 \]

Airside of dual exposure sample

Both sides exposed to air+3%H₂O
Crofer 22 APU: Effects of Water Vapor

To air+3%H₂O at both sides.

(Air+3%H₂O) side of dual exposures.

Surface microstructures

Cross-sections

Fe₂O₃-rich nodules

Fe

Cr

Mn
Crofer22 APU: Effects of Thermal Cycling

Grown on the Crofer22 APU coupon in air only and at the airside of the coupon that was heat-treated at 800°C, three cycles with each cycle of 100 hours.

M = Fe-Cr Substrate
C = Cr₂O₃
S = (Mn,Cr,Fe)₃O₄
O = Fe₂O₃

Airside of the dual exposures.

Air exposure at both sides.
Crofer22 APU: Effects of Thermal Cycling

To air at both sides

Airside of dual exposures

Surface microstructures

Cross-sections

Fe2O3

Mn

Cr

Fe

Airside of dual exposures

Surface microstructures

Cross-sections

Fe

Cr

Mn
Crofer22 APU: Effects of Temperature

Grown on the airside of the Crofer22 APU that was heat-treated under the hydrogen/air dual exposures at 850°C for 300 hours.
Effects of Cr%: AISI430 (17% Cr)

Grown on the coupon in air only and at the airside of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.
Effects of Cr%: E-brite (27% Cr)

Grown on the coupon in air only and at the airside of the coupon that was **ISOTHERMALLY** heat-treated at 800°C, 300 hours.

- **Air exposure at both sides**
- **(H₂+3%H₂O) at both sides**
- **Air side of dual atmospheres**
- **Fuel side of dual atmospheres**
**Mechanism?**

**H/H⁺ Induced Anomalous Oxidation**

\[ \text{H} + \text{O}_\text{O}^x + h^\bullet = (\text{OH})_\text{O}^\bullet \]

\[ [h^\bullet] + [(\text{OH})_\text{O}^\bullet] = 3[V_M^\text{Ov}] \]
Oxidation Study under Reformate||Air Dual Exposures

Materials studied:

- Alloy composition
  - E-brite-27%Cr
  - Crofer22-22%Cr
  - AISI430-17%Cr

Fuel side:

- Metal substrate
- $p_{H_2}$
- $p_{H_2O}$
- 74%H$_2$
- 9.7%H$_2$O
- 3%H$_2$O
- 9.8% CO, 6.2% CO$_2$

Air side:

- Air
- Metal substrate
- $p_{H_2}$
- $p_{H_2O}$
- 74%H$_2$
- 9.7%H$_2$O
- 3%H$_2$O

Diagram showing air flow and fuel flow with temperature and pressure readings.
Oxidation Behavior at Airside

M = Fe-Cr substrate
C = Cr₂O₃
S = (Mn,Cr)₃O₄
H = α-Fe₂O₃

Nucleation of Fe-rich nodules
Oxidation Behavior: Air Only vs. Dual

Air exposure at both sides

Airside of dual exposures

Surface microstructures

Cross-sections
Scale Growth at Fuel Side

- M = Fe-Cr substrate
- C = Cr$_2$O$_3$
- S = (Mn, Cr)$_3$O$_4$
- Mc = M$_x$C$_y$

Intensity (a.u.)

Mc = M$_x$C$_y$?
Conclusions

The DUAL exposures lead to an anomalous oxidation behavior of high temperature oxidation resistant alloys under the SOFC interconnect dual exposure conditions:

- For ferritic stainless steels particularly with relative low Cr%, dual exposures enhance the iron transport in the scale on the airside, leading to hematite formation and localized attack;
- Thermal cycling further accelerates the iron oxide formation and attack;
- Under the reformate||air dual exposures, hydrogen and water gradient across Crofer22 APU enhance the anomalous oxidation at the airside of the metal.
- Further study needs to clarify the effects of carbon potential at the fuel side.
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