Low-Cr Fe-Ni-Co Alloys as Interconnect for Intermediate-Temperature SOFC

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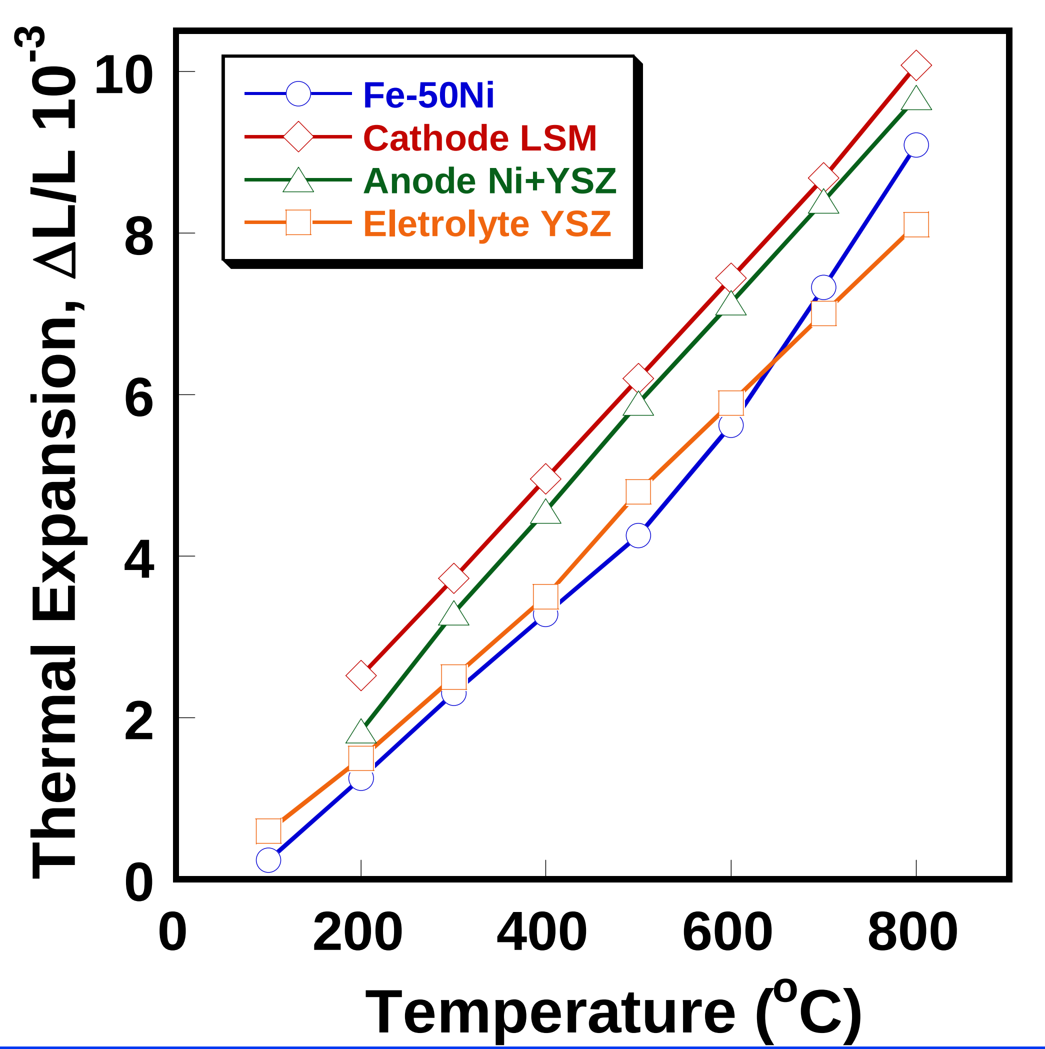
Why Cr-free or low Cr alloys as solid oxide fuel cell (SOFC) interconnect material?

- Currently, the metallic interconnects for intermediate-temperature SOFC are the Cr_2O_3-forming alloys such as Ebrite, Crofer, and Haynes 230 due to the electrically conductive nature of Cr_2O_3 compared to Al_2O_3 and SiO_2.
- However, an inherent weakness of Cr_2O_3-forming alloys is the formation of volatile Cr species due to chromium evaporation, which will migrate to and thus poison the cathode, resulting in SOFC performance degradation
- Two approaches can be taken to address this issue:
  - ✓ *Surface coating approach*
  - ✓ *Alloy design approach*

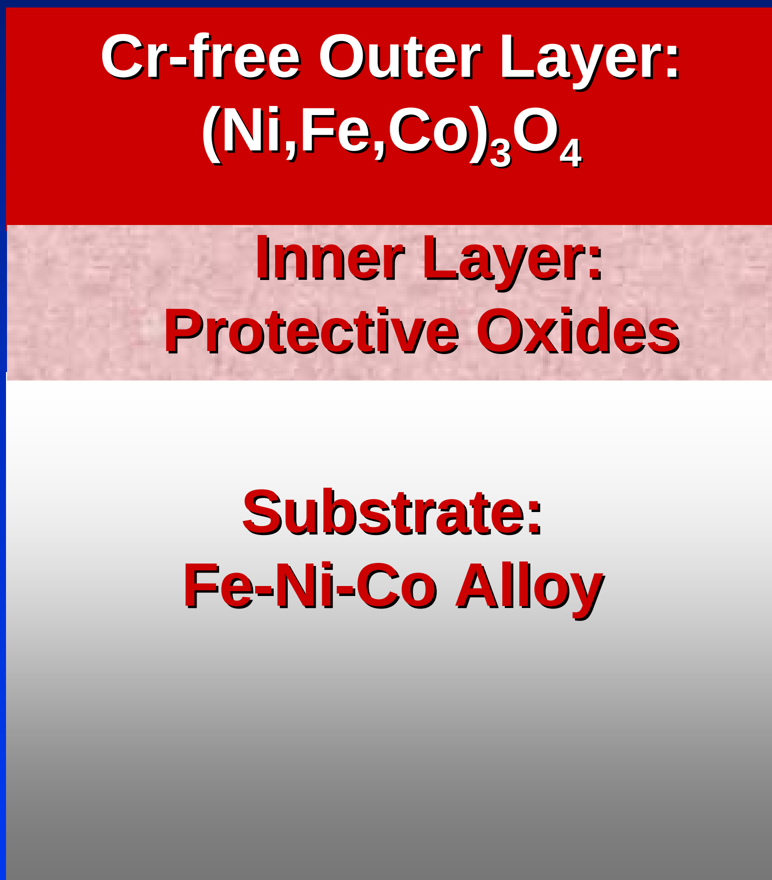
Cr-free or low Cr Fe-Ni-Co alloys tailored for SOFC interconnect application might completely resolve the Cr poisoning issue in SOFC stacks without the need of a surface coating.

Why Fe-Ni-Co Alloys as SOFC Interconnect?

- **Features of Fe-Ni and Fe-Ni-Co alloys:**
  - Low CTE due to the "Invar" effect
  - No Cr or low Cr content for lowering Cr volatility
  - Poor oxidation resistance at SOFC operating temperature
- **Potential exists for further development for SOFC interconnect application.**



Alloy Design of New Fe-Ni-Co Base Alloys Forming Double-Layer Oxide Structure During Oxidation



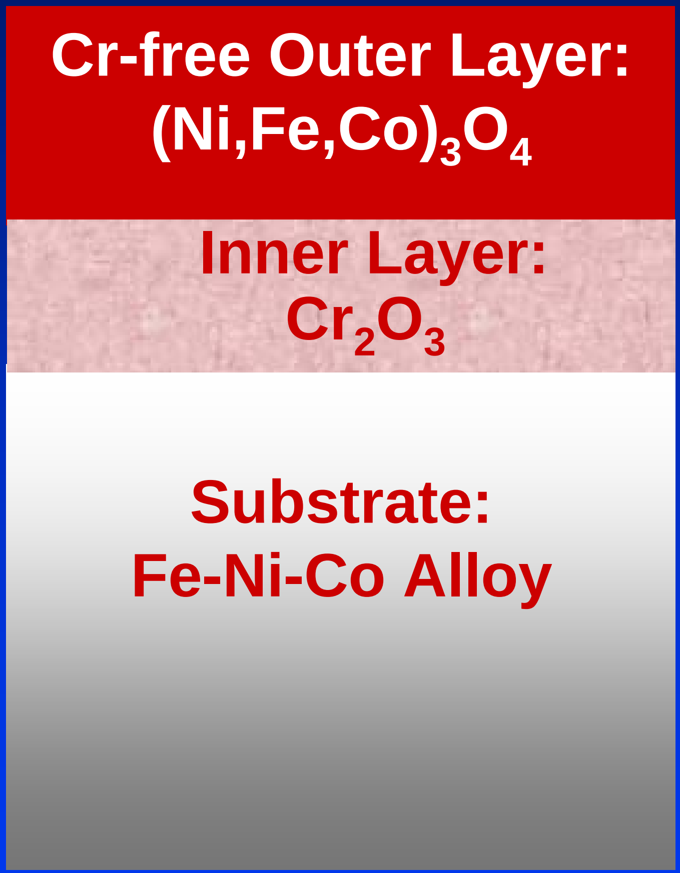
Schematic of Thermally-Grown Double-Layer Oxide Structure

In addition to providing electron conduction path, these attributes are desired:

- **Provide low Cr-volatility surface seal**
- **Provide oxidation diffusion barrier**
- **Provide CTE match with other cell components**

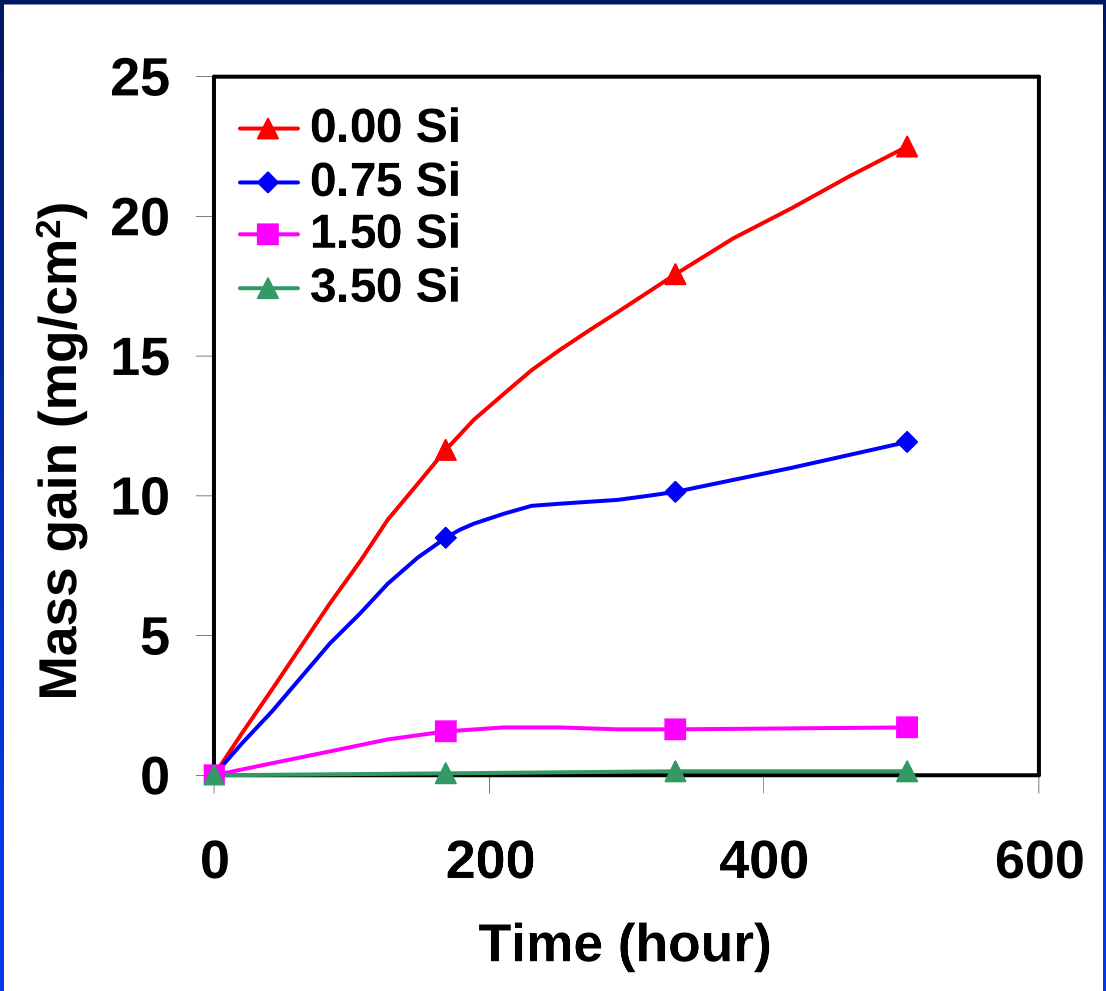
Alloy Design Philosophy for the New Fe-Ni-Co Alloy System

- The alloy composition of Fe-25Ni-30Co- 6Cr-5Nb-1.5Si-0.1Y was designed to give an overall optimal property:
  - Co: further modify the alloy CTE and the conductivity of the spinel
  - Cr: improve the oxidation resistance (increases the alloy CTE)
  - Nb: reduce the CTE of the alloy and form Nb-Si compound
  - Si: enhance oxidation resistance and strengthen the alloy via the formation of the Nb-Si compound



Double-layer concept for protecting the alloy

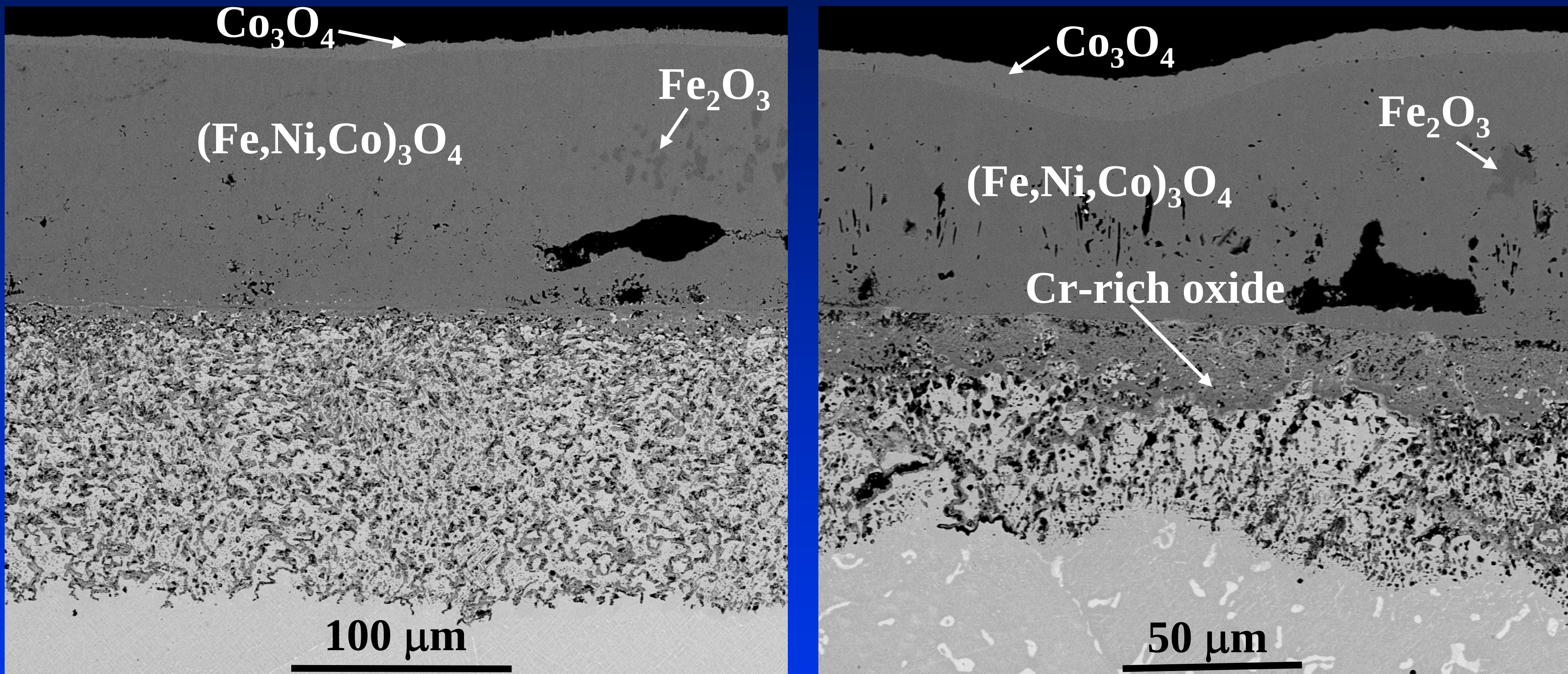
Effect of Si (wt.%) on the Oxidation Behavior of Cast Low-Cr Fe-Ni-Co Alloys in Air at 800°C



Oxidation kinetics of low-Cr Fe-Ni-Co alloys with different Si levels at 800°C in air

- The mass gain of the alloys decreased with the increase in Si content in the Fe-Ni-Co alloys

Effect of Si on the Oxide Structure of Low-Cr Fe-Ni Alloys After Oxidation for 3 Weeks in Air at 800°C

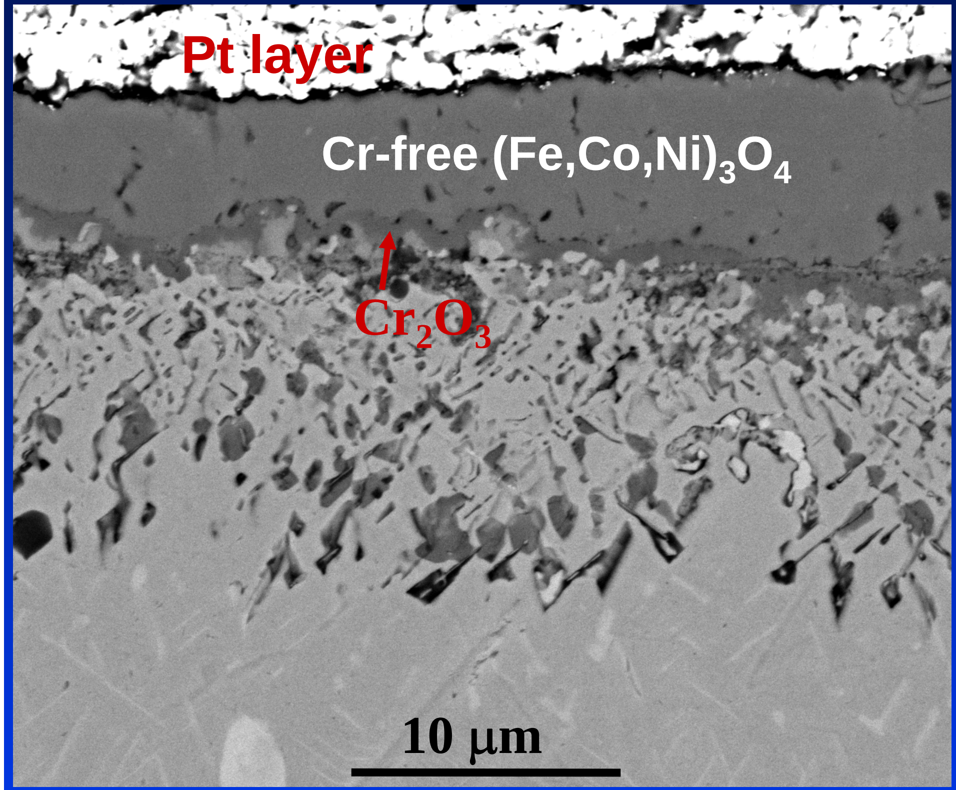


0% Si

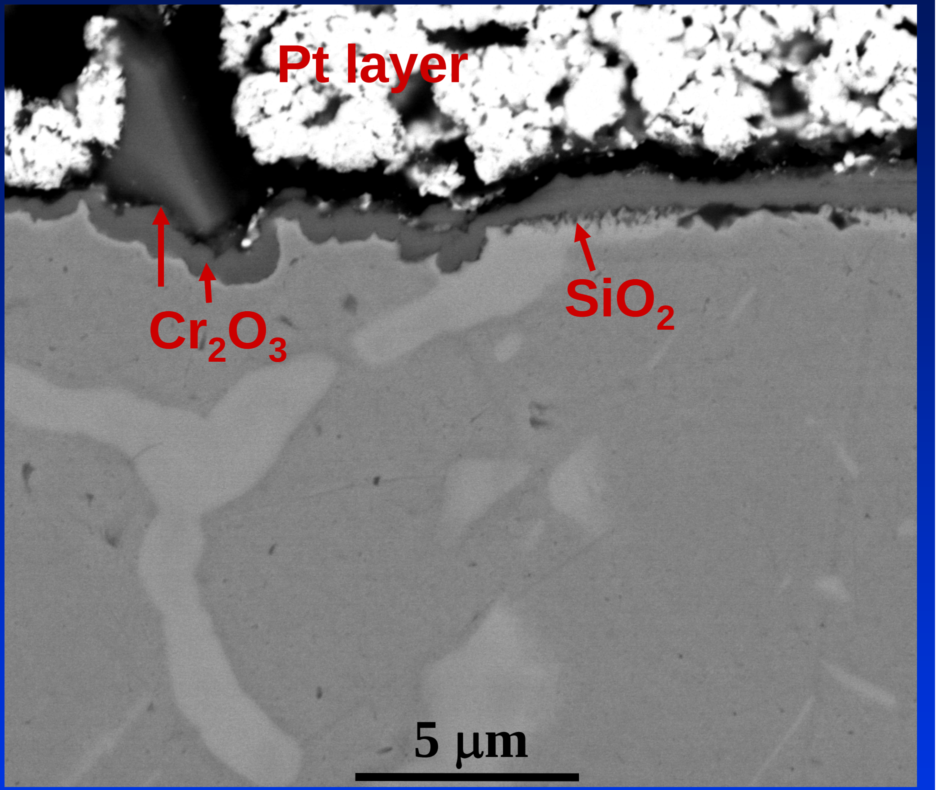
0.75% Si

- A surface Co_3O_4 spinel layer over a $(Fe,Ni,Co)_3O_4$ layer was observed for these two alloys.
- A significant amount of internal oxidation was observed.

Effect of Si on the Oxide Structure of Fe-Ni-Co Alloys After Oxidation for 3 Weeks in Air at 800°C



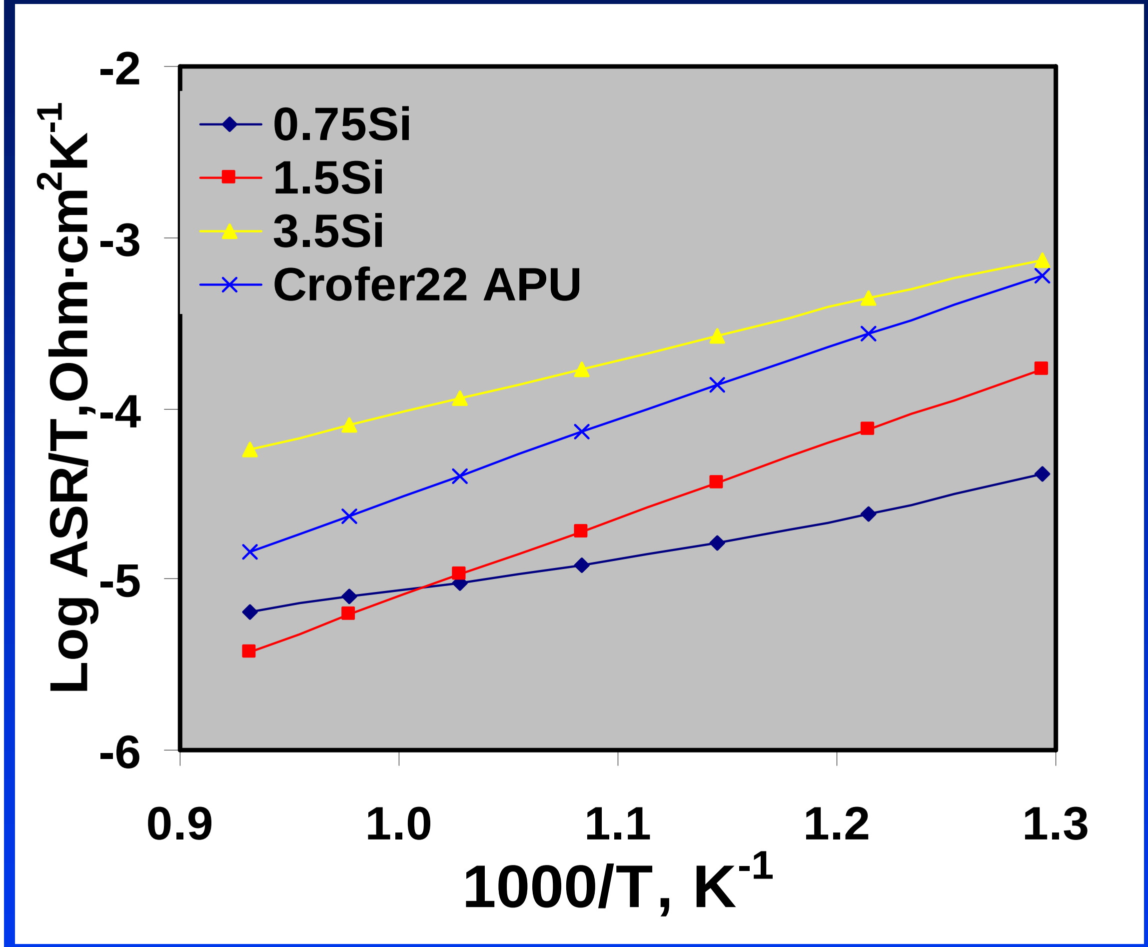
1.5% Si



3.5% Si

- Only $(Fe,Ni,Co)_3O_4$ spinel was observed for the alloy with 1.5%Si, with a Cr_2O_3 inner layer
- A continuous Cr_2O_3 surface layer was formed for the alloy with 3.5%Si, with some SiO_2 at the Si-rich precipitates.

Effect of Si on Scale ASR of Low-Cr Fe-Ni-Co Alloys

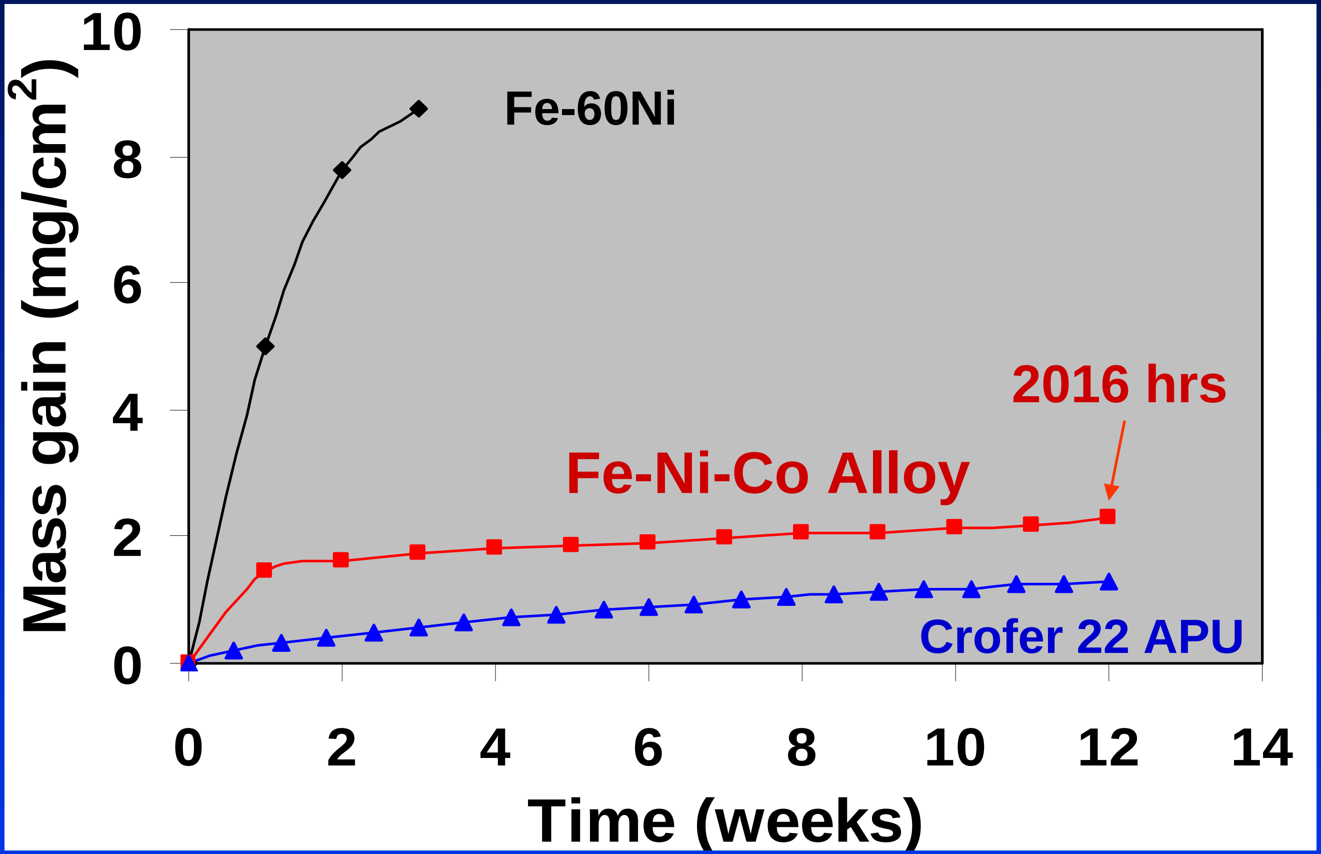


- The scale ASR increased with the Si content
- No continuous SiO_2 formation - even with 3.5%Si addition, the scale ASR was still relatively low.
- The alloy with 1.5%Si exhibited lower scale ASR than was Crofer 22 APU.

Scale ASR after 3 weeks @ 800ºC, air

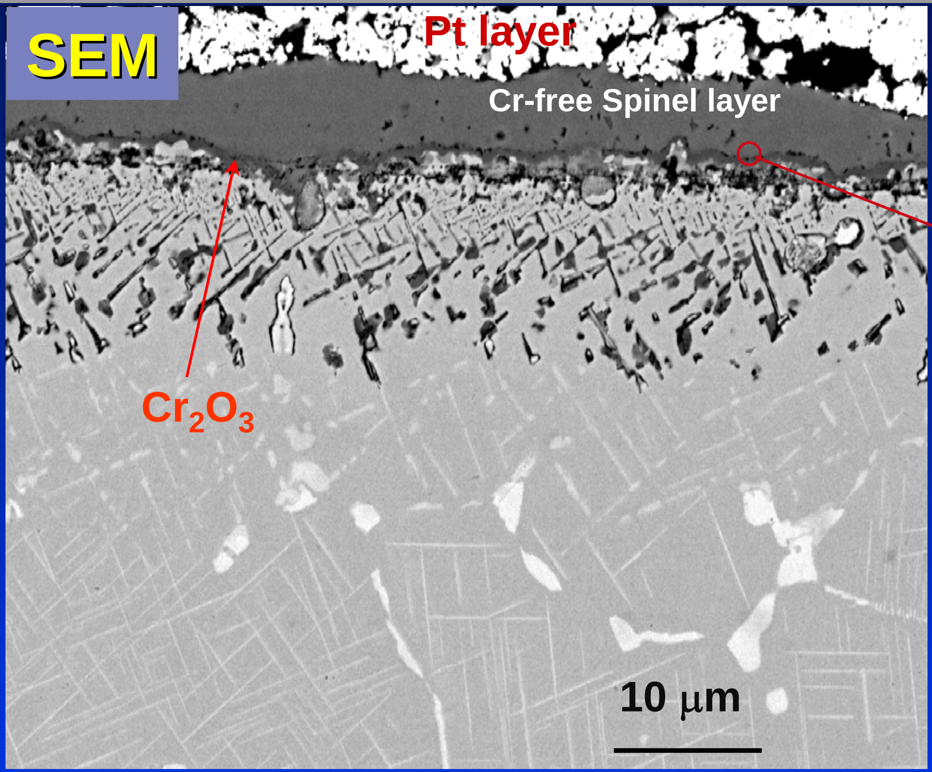
The alloy with 1.5%Si is selected as for further evaluation.

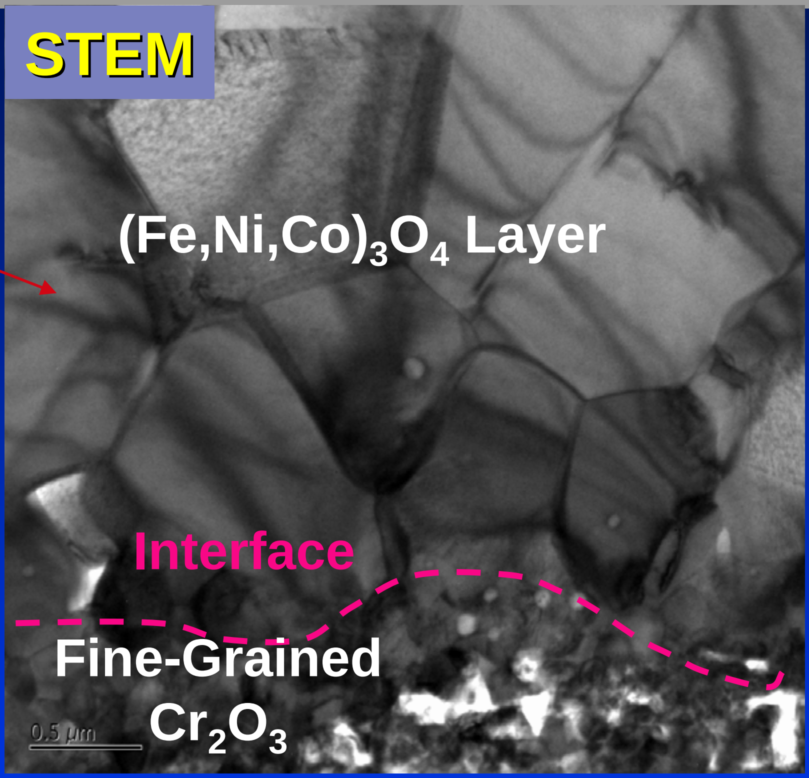
Isothermal Oxidation Kinetics of the Low-Cr Fe-Ni-Co Based Alloy in Air at 800°C



- After the 1st-week exposure, the oxidation rate of the Fe-Ni-Co alloy was similar to that of Crofer 22 APU.
- Large weight gain in the 1st week for the Fe-Ni-Co alloy was due to the *in-situ* formation of a Cr-free spinel layer.

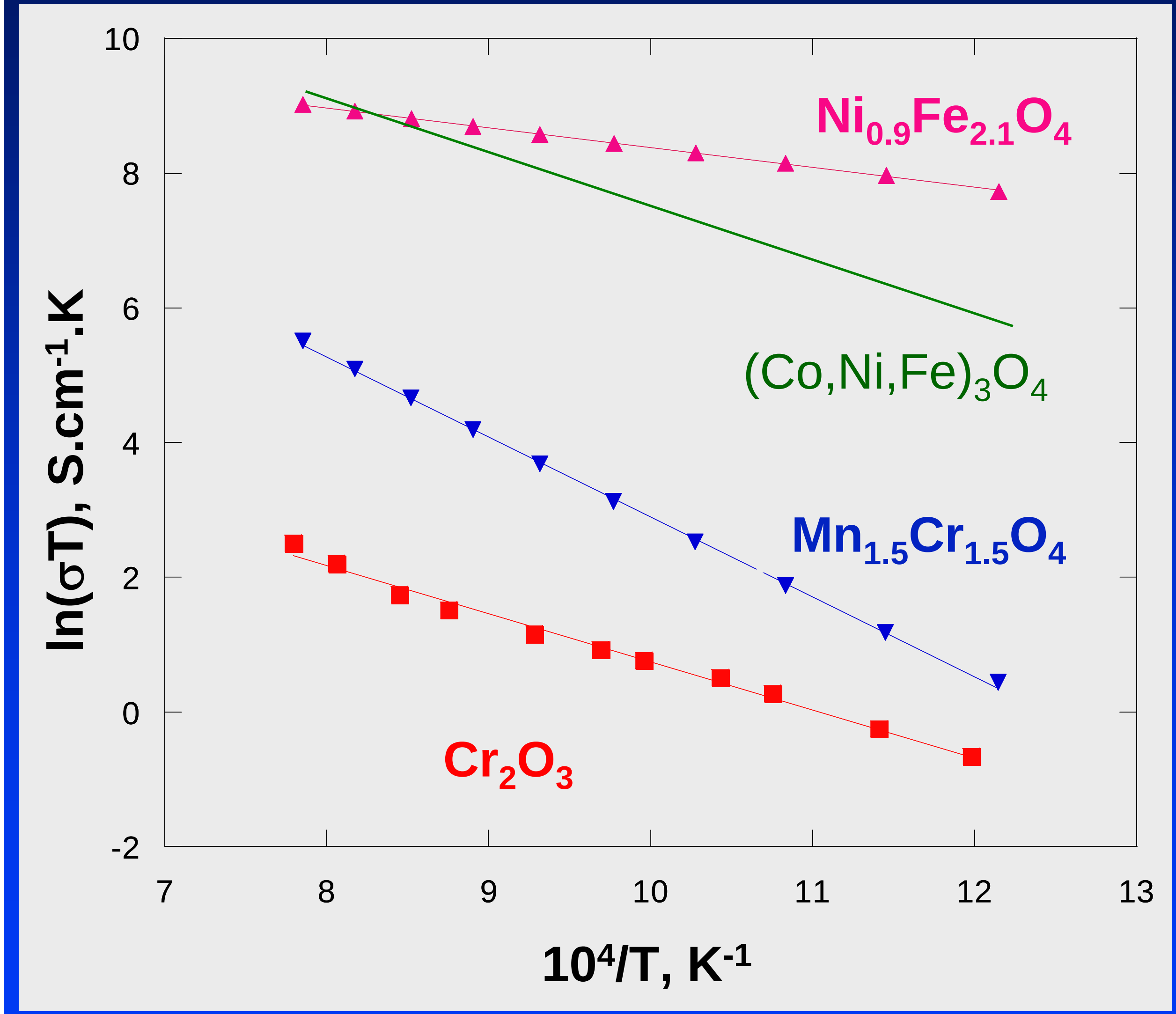
Cross-Sections of the Low-Cr Fe-Ni-Co Based Alloy after Oxidation for 3 Weeks at 800°C in Air





- The oxide scale formed on this alloy consisted of a Cr-free spinel outer layer and a fine-grained Cr_2O_3 inner layer
- An internal oxidation zone with mainly Cr_2O_3, $NbCrO_4$, Nb-Ni-Co-Si-O, etc.
- No continuous SiO_2 layer was detected.

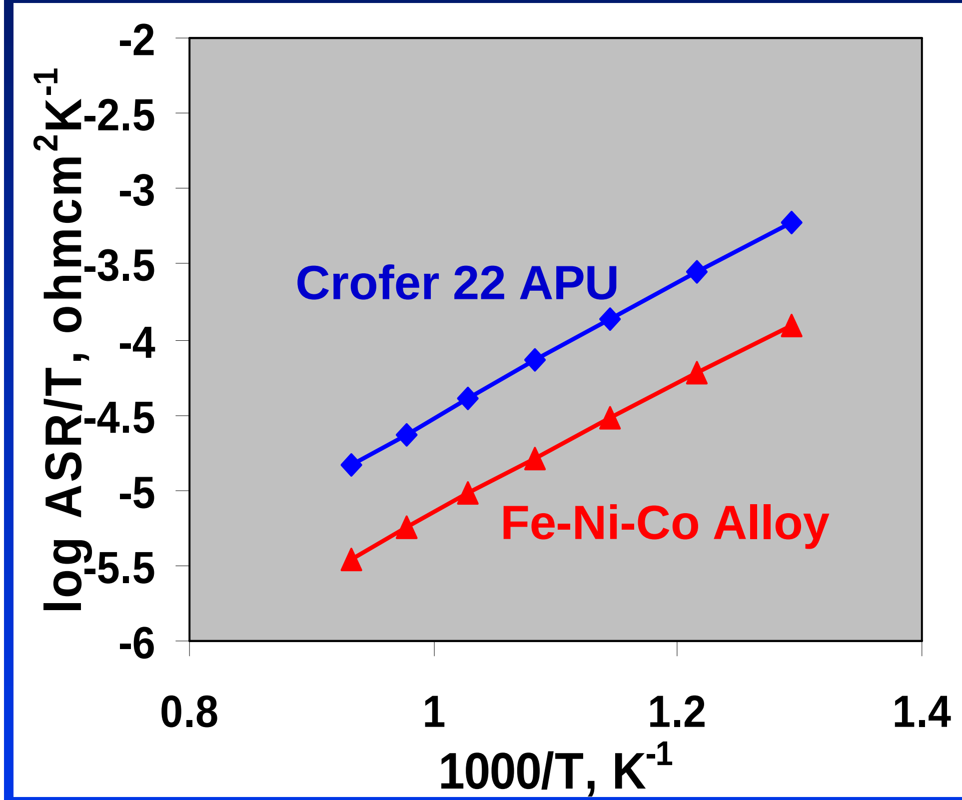
$Co_{0.84}Ni_{0.27}Fe_{1.89}O_4$ possessed similar electrical conductivity as $Ni_{0.9}Fe_{2.1}O_4$



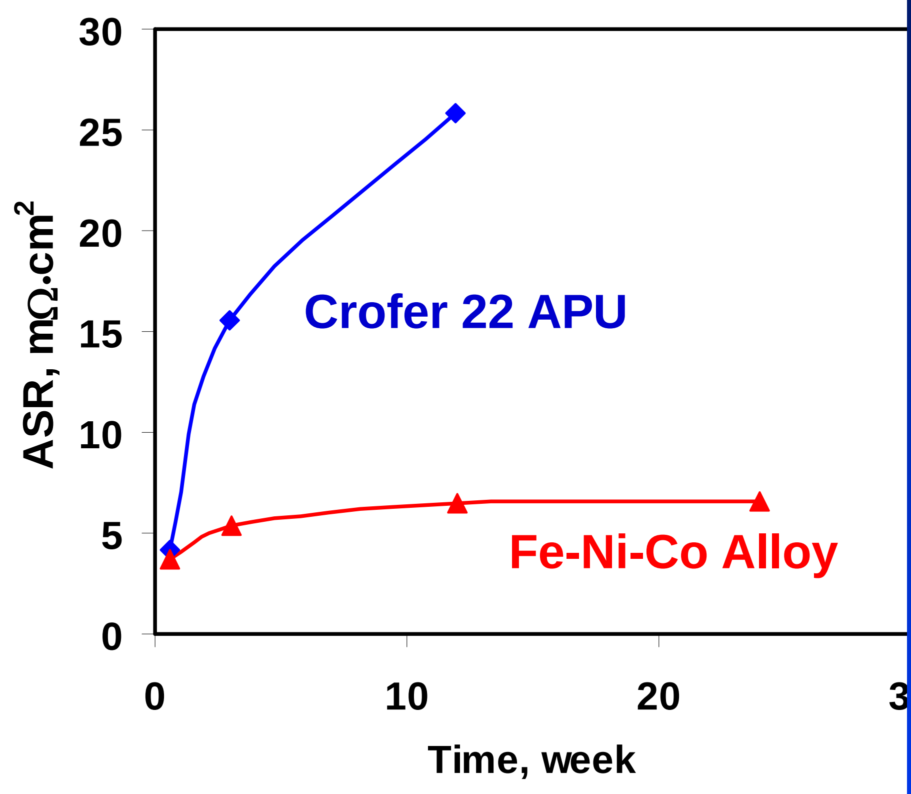
- ✓ $Ni_{0.9}Fe_{2.1}O_4$ similar to the spinel formed on Fe-Ni alloys
- ✓ $Mn_{1.5}Cr_{1.5}O_4$ similar to the spinel formed on Crofer (Fe-Cr-Mn)
- ✓ $Co_{0.84}Ni_{0.27}Fe_{1.89}O_4$ similar to the spinel formed on the new Fe-Ni-Co alloy

Scale ASR of the Low Cr Fe-Ni-Co Based Alloy after Oxidation at 800°C in Air

ASR vs. 1/T after 3-week Exposure



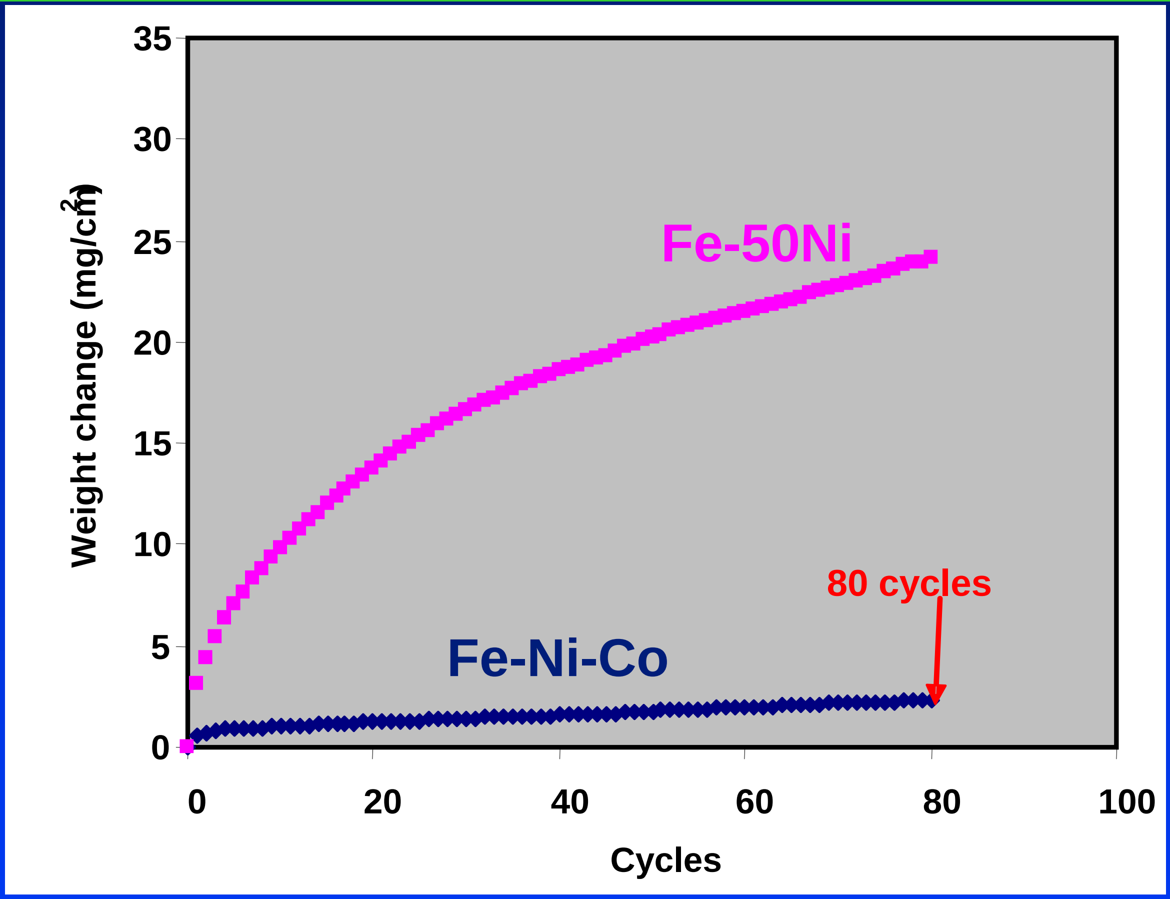
ASR at 800°C vs. Oxidation Time



- The scale ASR for the Fe-Ni-Co alloy after 3-week oxidation was lower than that for Crofer 22 APU
- The scale ASR was quite stable upon further oxidation

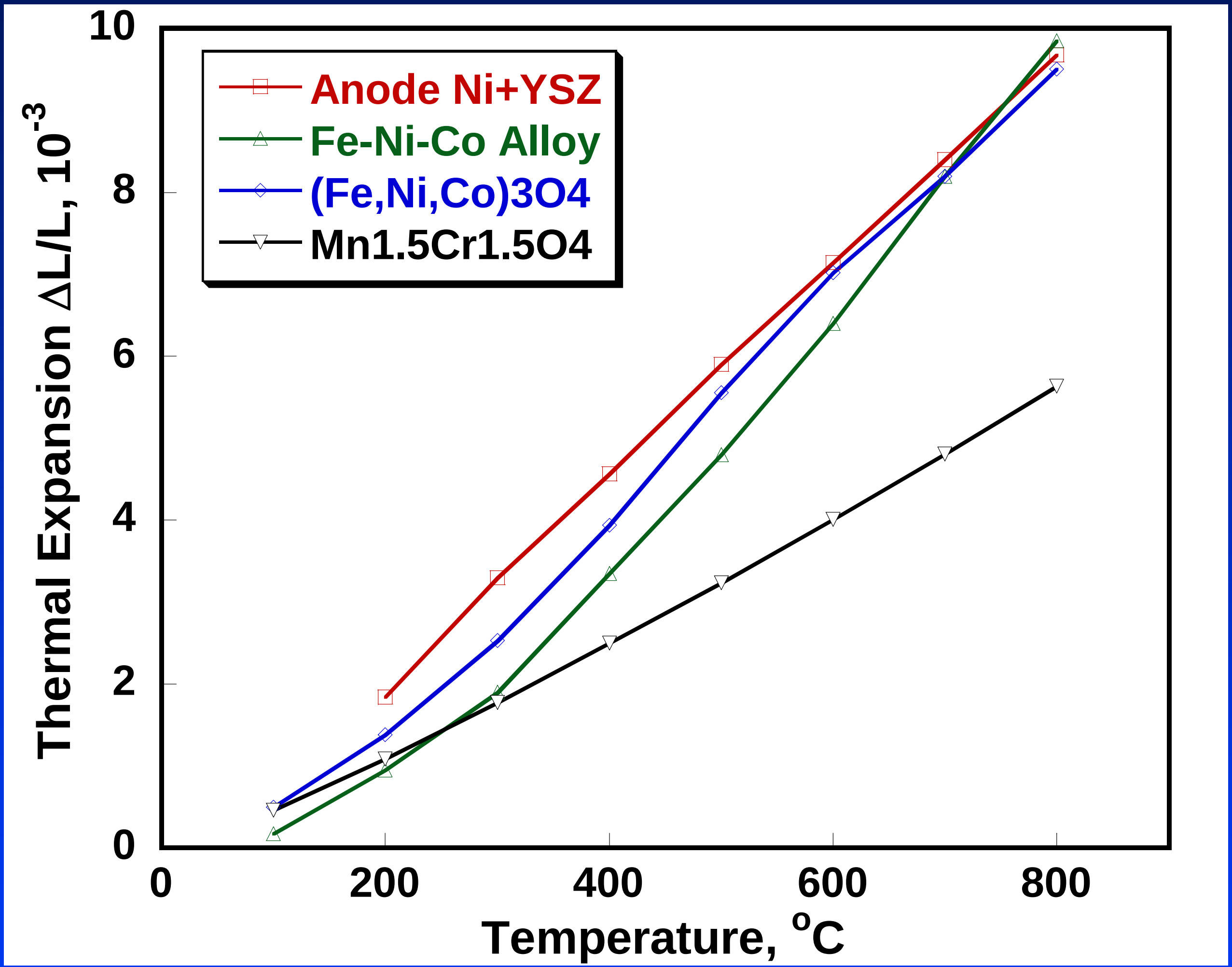
Cyclic Oxidation of the Low-Cr Fe-Ni-Co Alloy

Oxidation kinetics of two alloys after 80 cycles (25-h cycle, 800°C, air cooling)



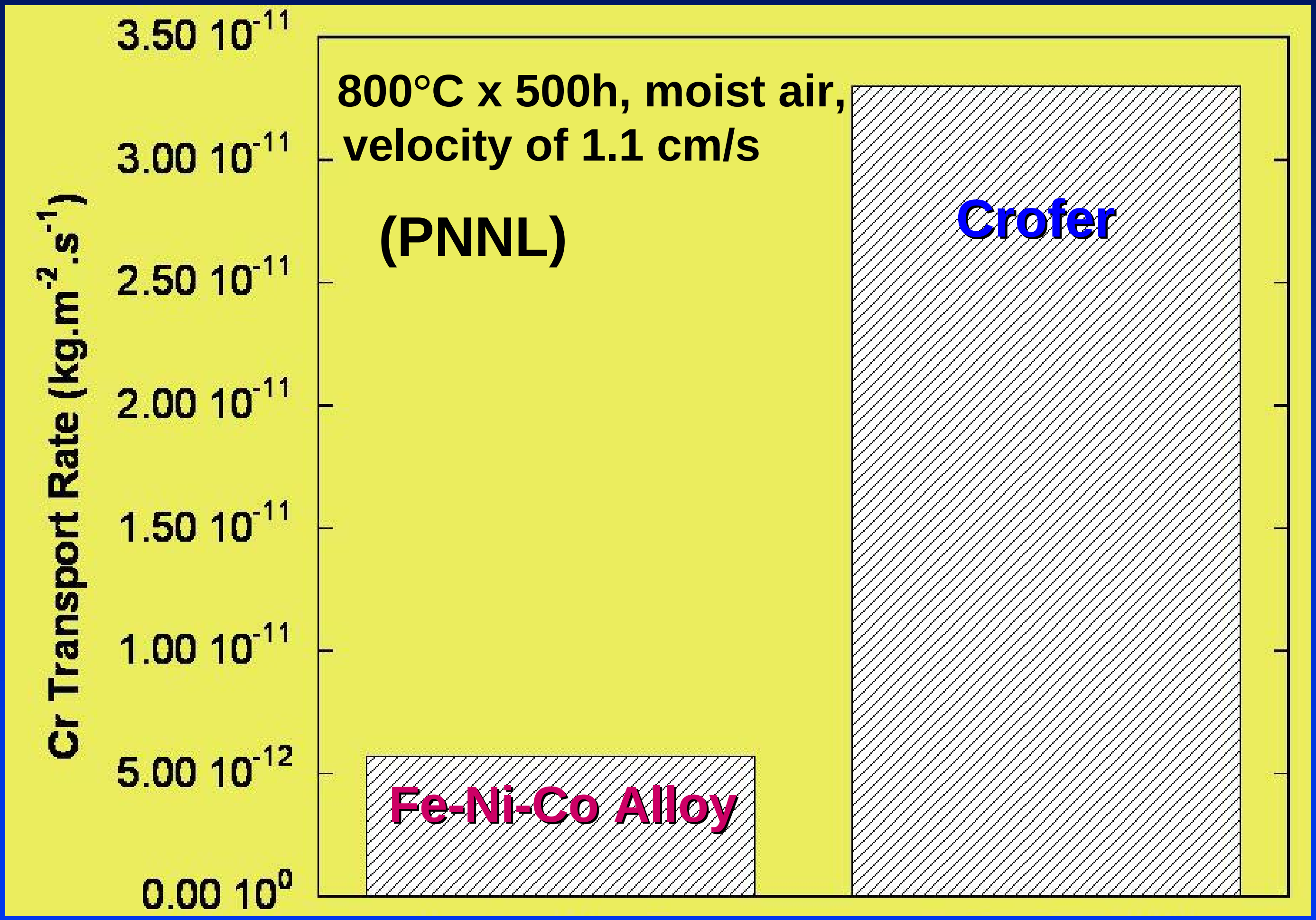
- **The good scale spallation resistance resulted from the excellent match in CTE of the oxide scale and the substrate**

Excellent Match in Thermal Expansion Between the Fe-Ni-Co Alloy and $(Fe,Ni,Co)_3O_4$ Spinel



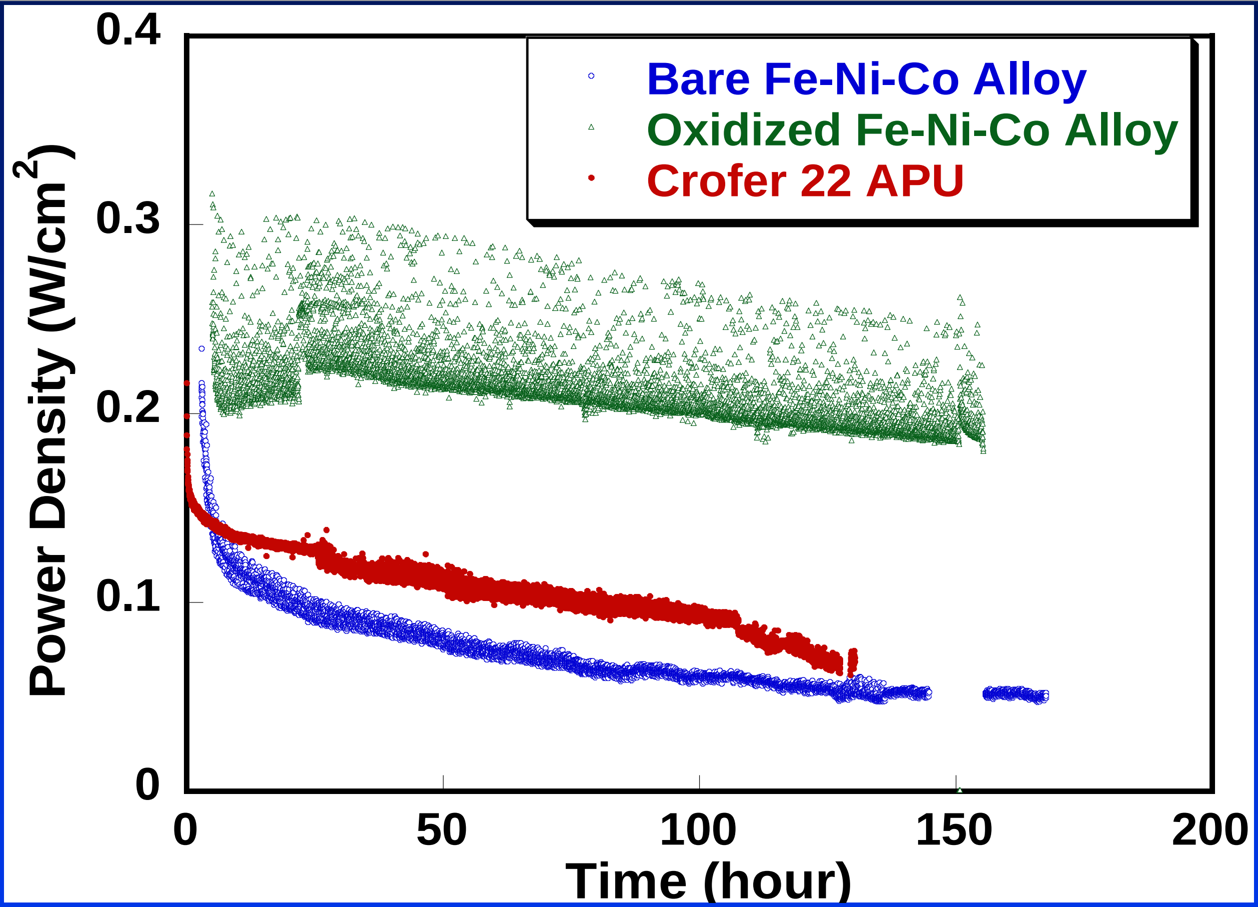
- The $(Fe,Ni,Co)_3O_4$ spinel layer formed on the Fe-Ni-Co alloys is expected to resist cracking during thermal cycling

Cr volatility of the Fe-Ni-Co alloy was much lower than that of Crofer 22 APU



- **The Cr-free spinel outer layer formed on the Fe-Ni-Co alloy acts as a surface seal to effectively block the Cr evaporation**

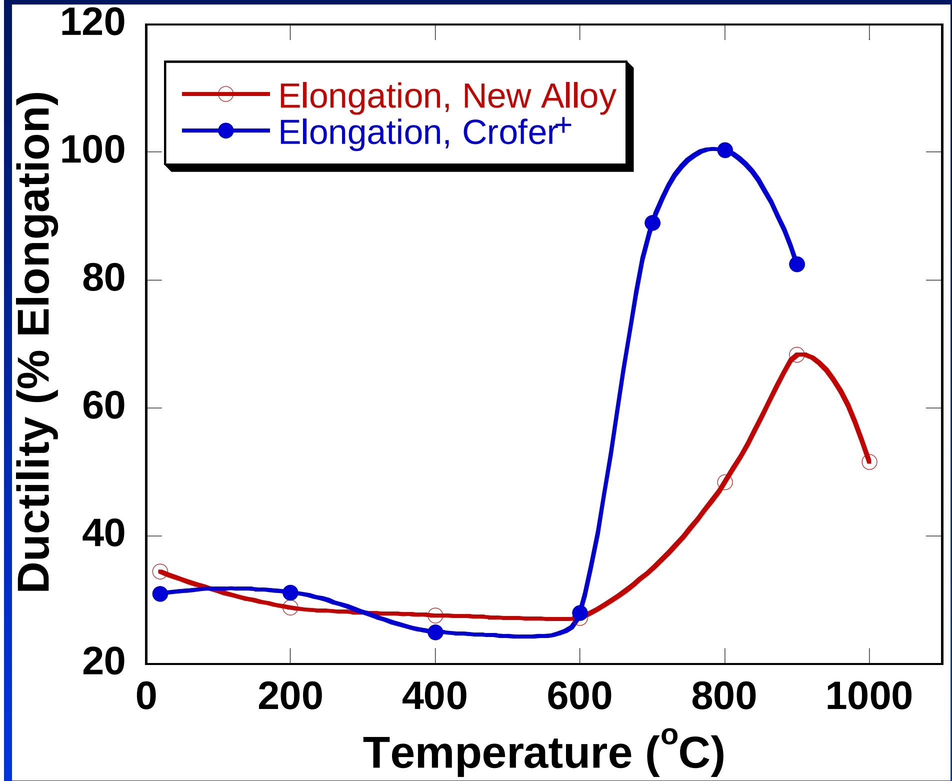
In-Cell Testing Results with the Fe-Ni-Co Alloy Interconnect

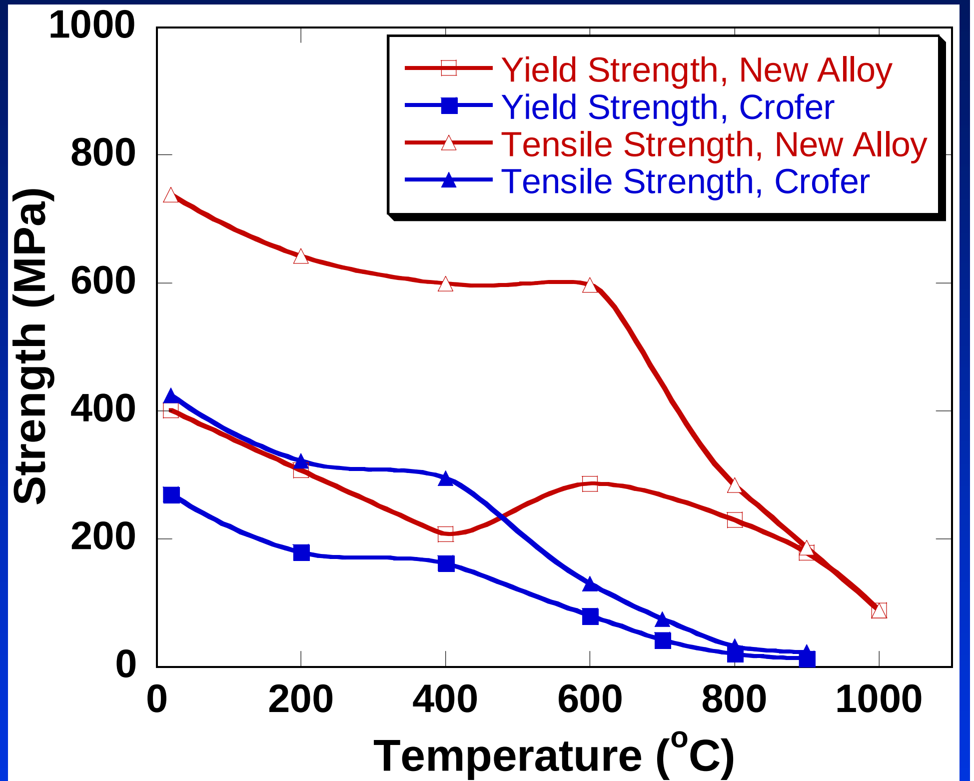


Cell Configuration:
Alloy/Pt/LSM/LSM+YSZ/YSZ/Ni+YSZ
Test Condition:
800ºC at 0.7V
50 sccm Moist H_2
750 sccm Air
Interconnect:
1.2mmx1.2mm
$2.5cm^2$ active area

- Cell performance degradation rate with the Fe-Ni-Co alloy interconnect was similar to Crofer 22 APU at 800°C initially.
- Preoxidation at 800°C in air for 120 hours significantly reduced the cell degradation due to the formation of the spinel layer.

Tensile Properties of the New Fe-Ni-Co Alloy (Hot- + Cold-Rolled, 1000°Cx1h, 800°Cx10h)





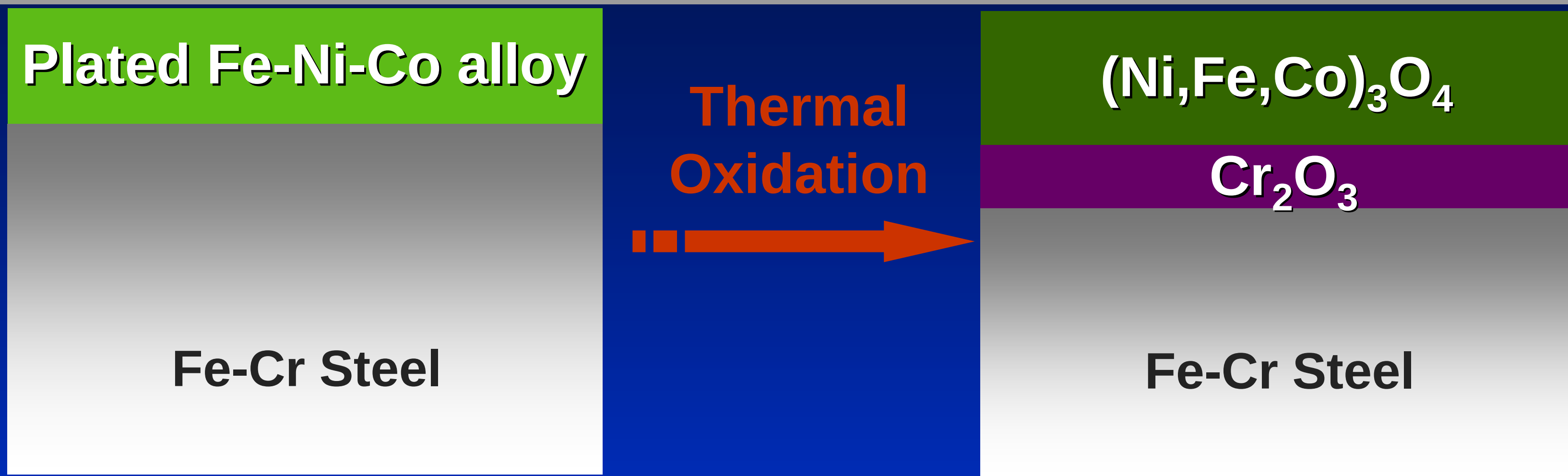
- The ductility of the new alloy was similar to Crofer 22 APU up to 600°C and slightly lower in the range of 600-900°C.
- The new alloy exhibited a much higher yield strength and tensile strength over the entire test temperature range.

+Data for Crofer 22 APU was from R. Hojda & L. Paul, NACE Paper No. 6479, Corrosion 2006.

Current/Future Research Directions

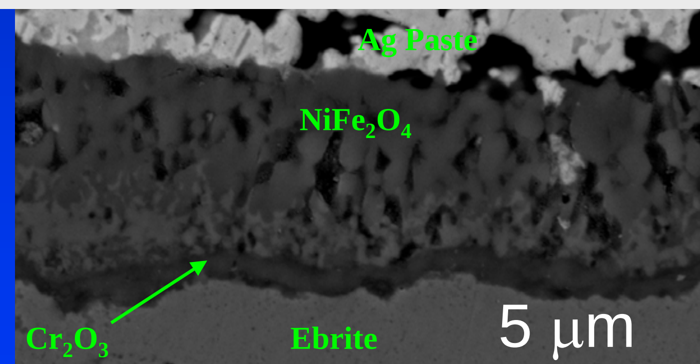
- Alloy Development
  - Further Optimization of Alloy Compositions
  - Evaluation of Other Properties (Forming, Creep, etc.)
- Coating Development for Cost Reduction
  - Electroplating of the Fe-Ni-Co Alloy on Ferritic Steels as a Precursor for Synthesizing the $(Fe,Ni,Co)_3O_4$ Spinel Coating
  - Other Coating Processes such as Cladding, Screen Printing, etc.

Electroplating of the Fe-Ni-Co Alloy on Ferritic Steels to Achieve the Spinel Coatings



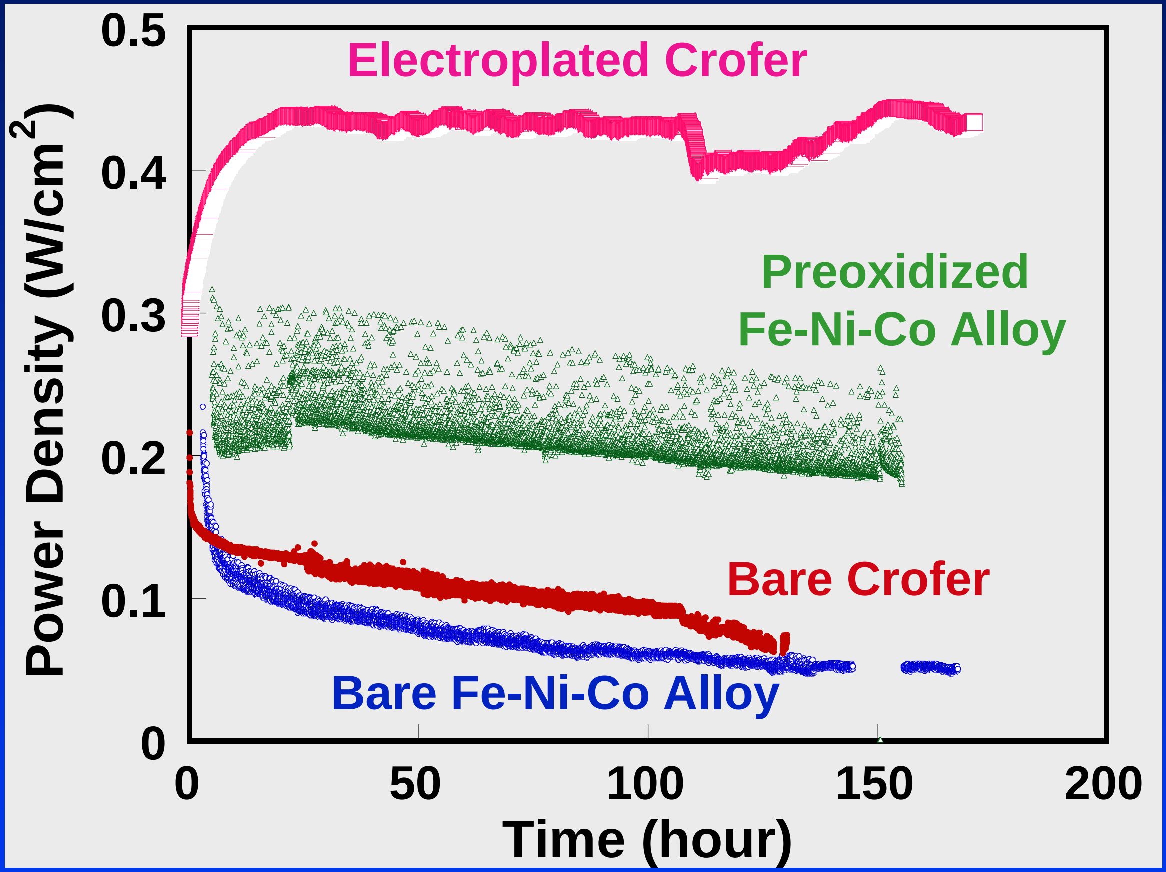
- Codeposition of a Ni-Fe-Co alloy layer on the ferritic steels via electroplating
- Oxidation in air can be used to convert the alloy into the spinel layer with the simultaneous formation of a Cr_2O_3 sub-layer

Electroplating: 20mA/cm^2, 40min
Thermal oxidation: 800°Cx1week



TTU's Electroplating Process: High Stability (>30 days, > 30 runs); Accurate Control of Coating Composition.

In-Cell Testing Results with Electroplated Crofer 22 APU Interconnect



- The electroplated Fe-Ni-Co layer on Crofer 22 APU significantly improved the cell stability, indicating its effectiveness in blocking the Cr migration.

Summary

- **CTE (√)**

  The CTE of these alloys matches other cell components.

- **Oxidation Resistance (√)**

  Effective alloying elements have been identified that significantly improve oxidation resistance of these alloys.

- **ASR (√)**

  The ASR of the oxide scales formed on the new alloys is comparable to that of current interconnect alloys.

- **Cr Volatility (√)**

  The Cr transport rate for the new alloys is much lower than that of Crofer 22 APU.

A series of low-Cr Fe-Ni-Co alloys have been developed that form a conductive, Cr-free spinel outer layer atop an Cr_2O_3 inner layer during thermal oxidation.

Acknowledgements

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