Tailoring Fe-Ni Based Alloys for Intermediate Temperature SOFC Interconnect Application[+]

[+]AGREEMENT NO. DE-FC26-04NT42223, START DATE OCT. 1, 2004

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SECA Core Technology Program Peer Review Meeting

October 25-26, 2005

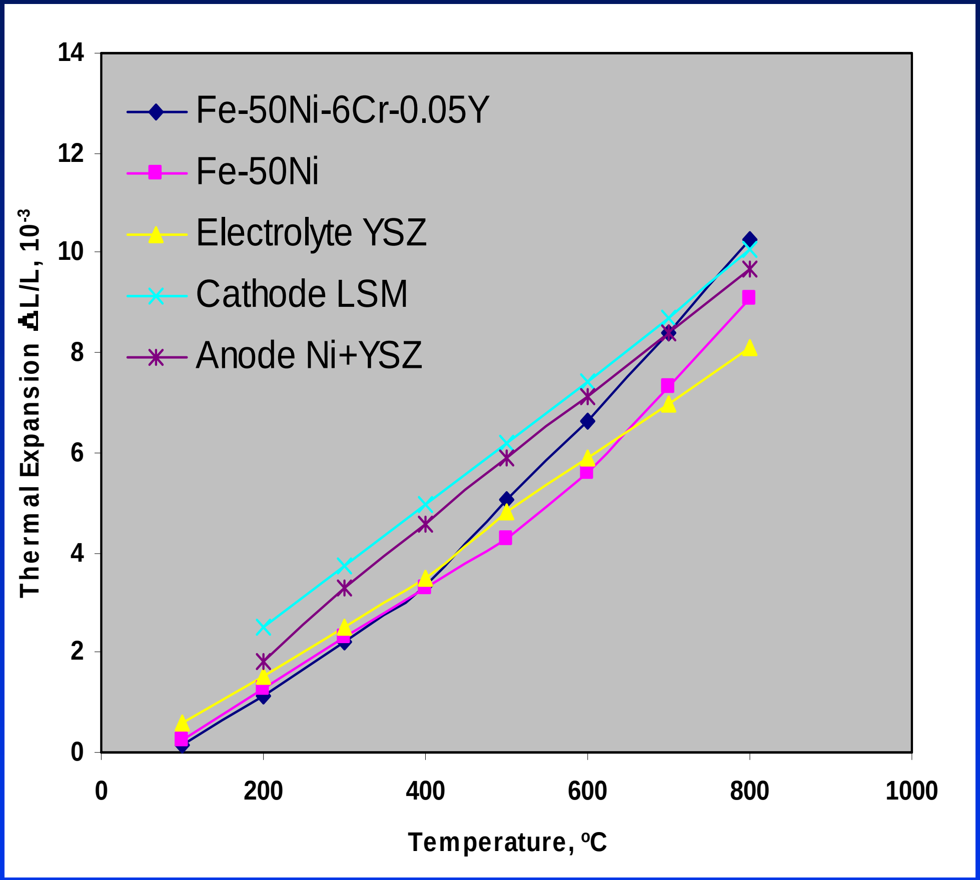
Why Cr-free or low Cr alloys as SOFC interconnect material?

- 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 alloys specifically tailored for SOFC interconnect application might completely resolve the Cr poisoning issue in SOFC stacks.

Cr-free or low-Cr Fe-Ni based alloys are potential interconnect materials for SOFC

- **Fe-Ni alloys with about 50 wt. %Ni exhibit thermal expansion behavior close to that of other cell components**
- **Fe-Ni alloys are Cr-free or low Cr, which is desirable to eliminate the Cr poisoning problem.**
- **The oxidation resistance and scale conductivity of the Fe-Ni based alloys might be tailored via alloy design**



Thermal Expansion vs. Temperature for the Fe-50Ni and Fe-50Ni-6Cr-0.05Y Alloys (wt.%), as Compared to Other Cell Components

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

- **CTE Match with Other Cell Components**

  Alloying additions such as Fe, Co, Ni, Mo, Nb, Ti, Cr, etc. will be controlled to maintain the CTE values of the new Fe-Ni based alloys at the desired level.

- **Oxide Scale Conductivity**

  In addition to control the Fe-Ni ratio, other transition metals will be identified and added to increase the electrical conductivity of the $NiFe_2O_4$ spinel layer.

- **Oxidation Resistance**

  An inner layer of dense, protective, and electrically conductive oxide (e.g. NiO, Cr_2O_3) will be formed after oxidation.

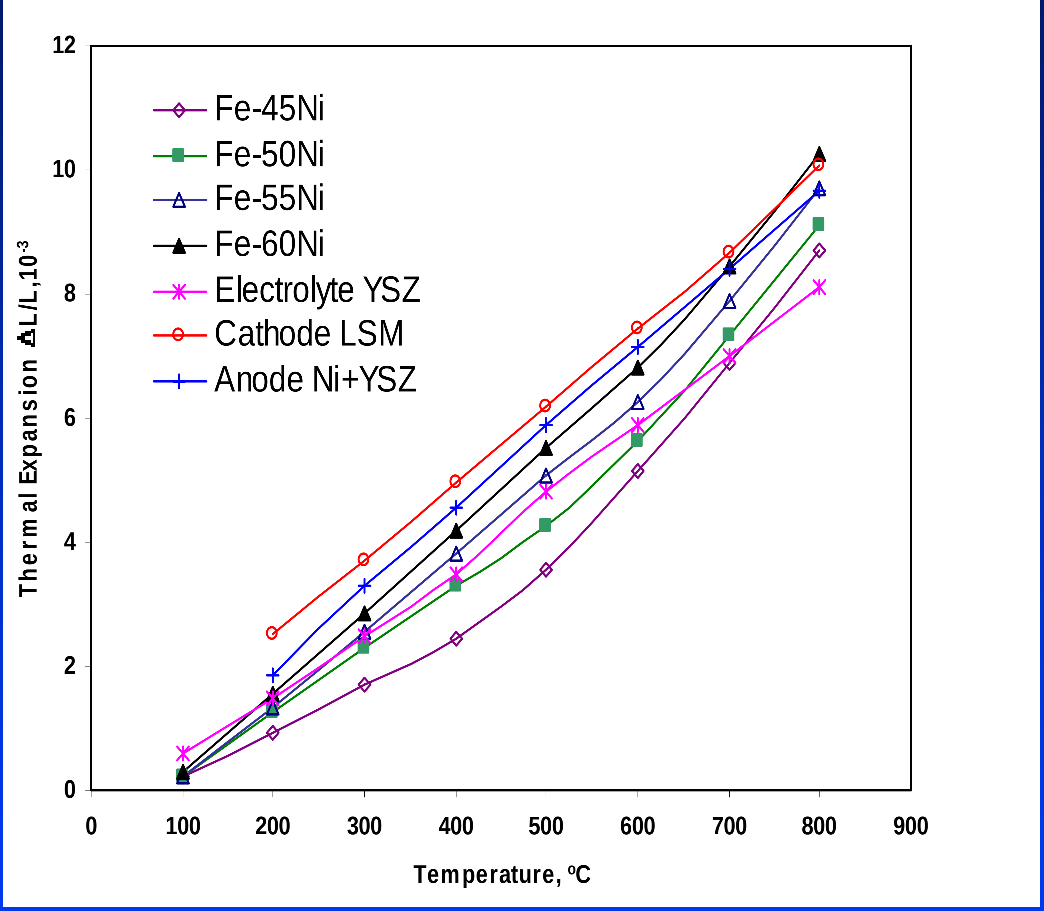
Schematic of the Desirable Double-Layer Oxide Structure

Binary Fe-Ni Alloys:
Identifying the Critical Issues

Low-Cr Fe-Ni Alloy Development:
Approach to Form the Desired Double-Layer Oxide Structure

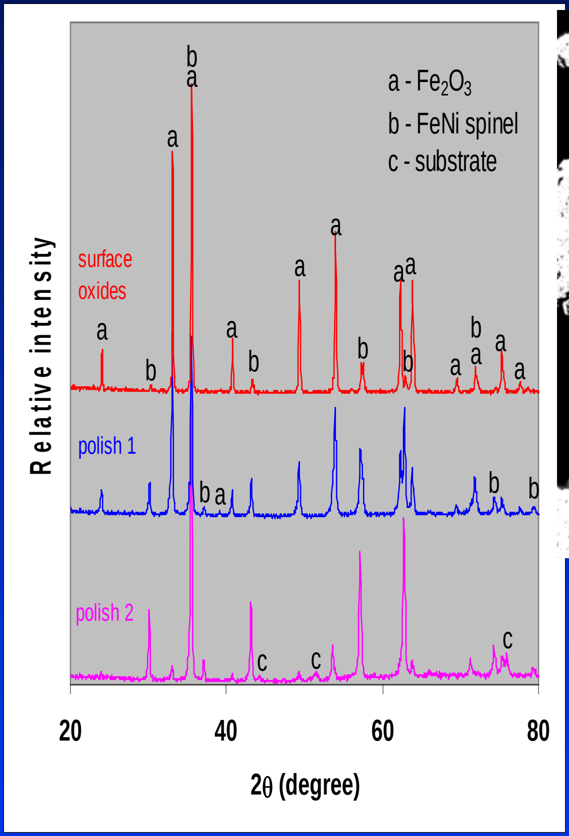
CTE of Cr-free Fe-Ni Binary Alloys

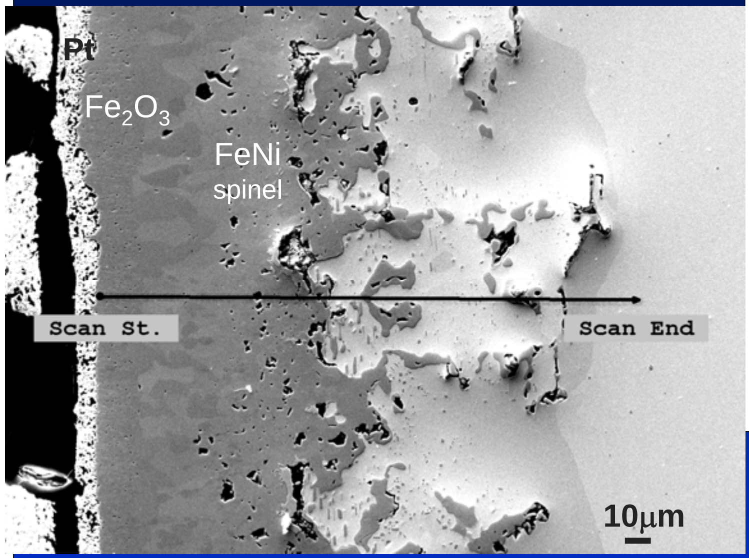
- The coefficient of thermal expansion (CTE) of binary Fe-Ni alloys with different Ni level (45-60wt.%) increased with the increase of Ni content.
- The thermal expansion behavior of the Fe-Ni alloys was close to that of other cell components.

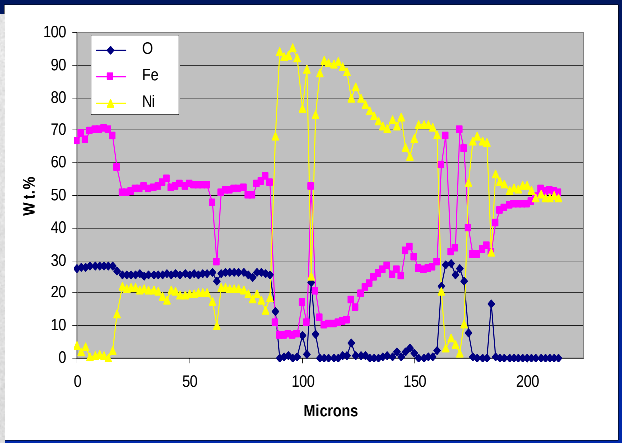


Thermal Expansion vs. Temperature for the Fe-Ni Alloys with Different Ni Content (wt.%), as Compared to Other Cell Components

EPMA was used to determine the spinel composition formed on the binary Fe-Ni alloys





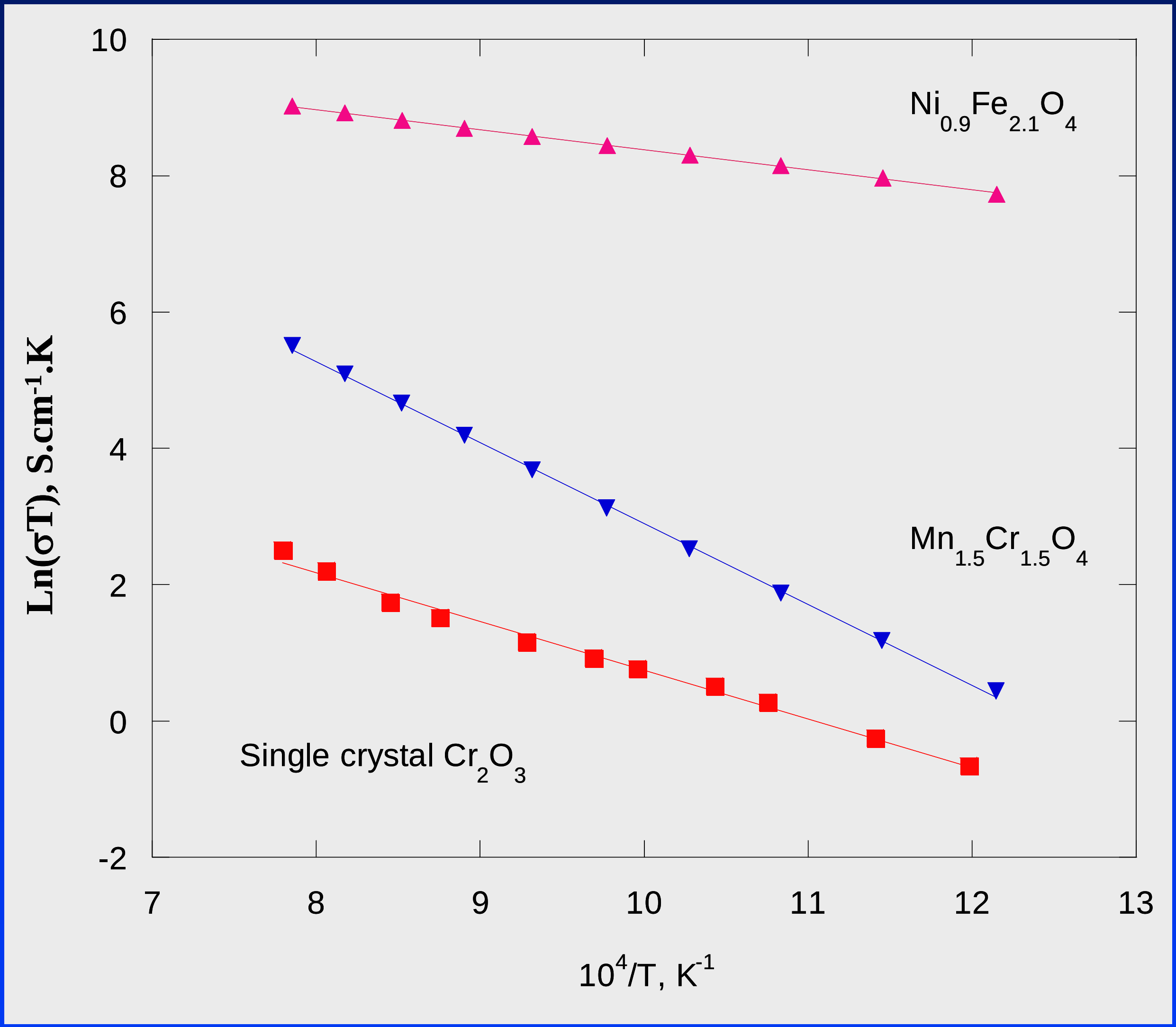


XRD patterns, cross-section, and electron-probe micro-analysis (EPMA) results of Fe-50Ni-0.05Y after oxidation for 500h in air at 800°C

Microns	At.%: O	Fe	Ni
46	55.4	33.2	11.4
48	56.0	32.6	11.4
50	55.1	33.2	11.7
52	55.6	32.8	11.6
54	55.4	32.7	11.9
56	55.4	32.7	11.9
58	55.7	32.6	11.7

- The surface oxide layer contained Fe_2O_3, which was in contact with a $Ni_{1-x}Fe_{2+x}O_4$ spinel layer.
- EPMA results indicated that the composition of the spinel was close to $Ni_{0.9}Fe_{2.1}O_4$.

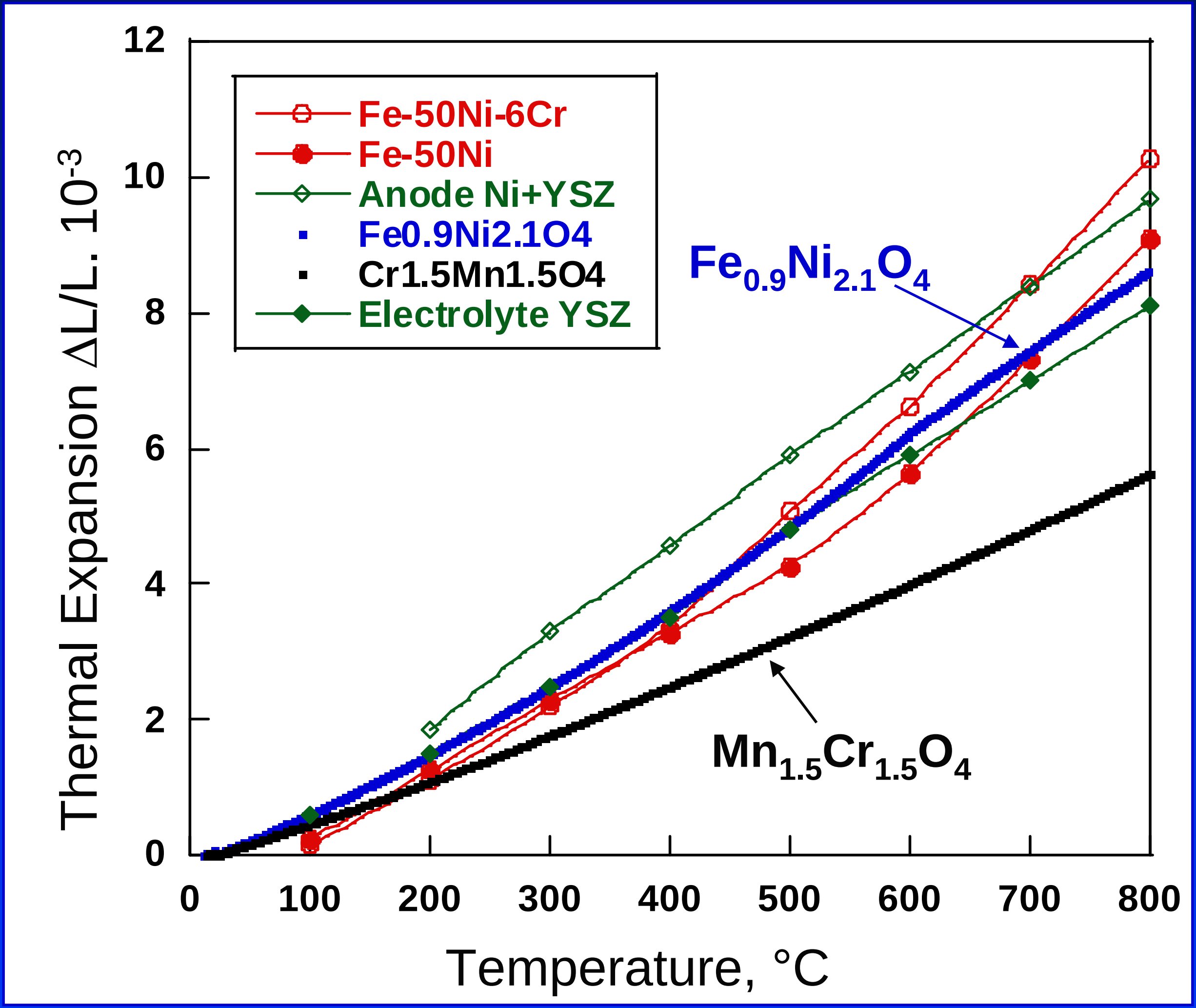
$Ni_{0.9}Fe_{2.1}O_4$ possessed much higher electrical conductivity than $Mn_{1.5}Cr_{1.5}O_4$ or Cr_2O_3



Dense pellets of $Ni_{0.9}Fe_{2.1}O_4$ and $Mn_{1.5}Cr_{1.5}O_4$ were used for electrical conductivity measurement (4-point DC technique):

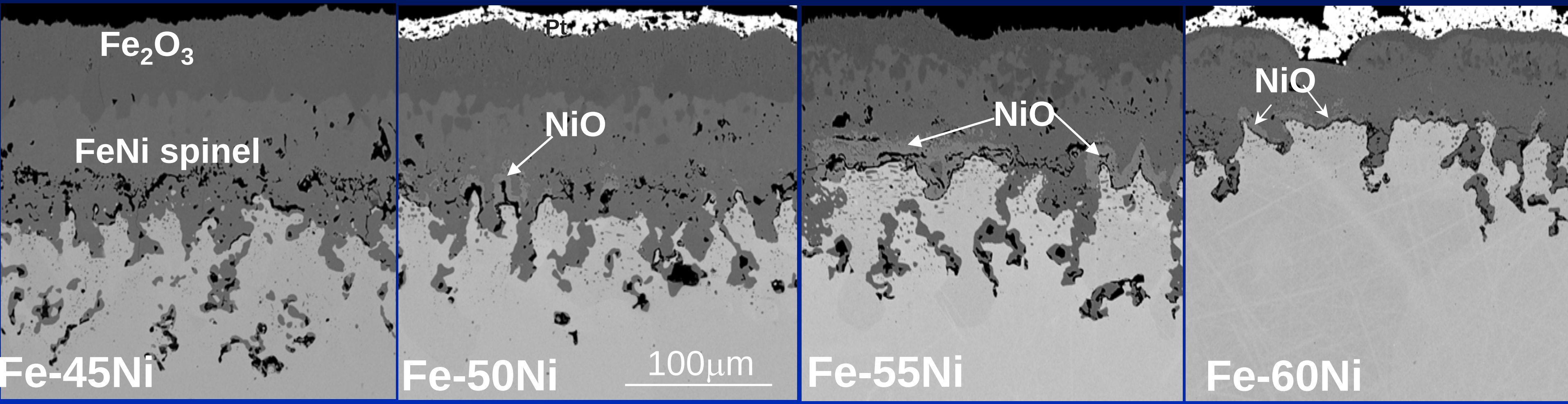
- ✓ **$Ni_{0.9}Fe_{2.1}O_4$ similar to the spinel formed on Fe-Ni alloys**
- ✓ **$Mn_{1.5}Cr_{1.5}O_4$ similar to the spinel formed on Crofer (Fe-Cr-Mn)**

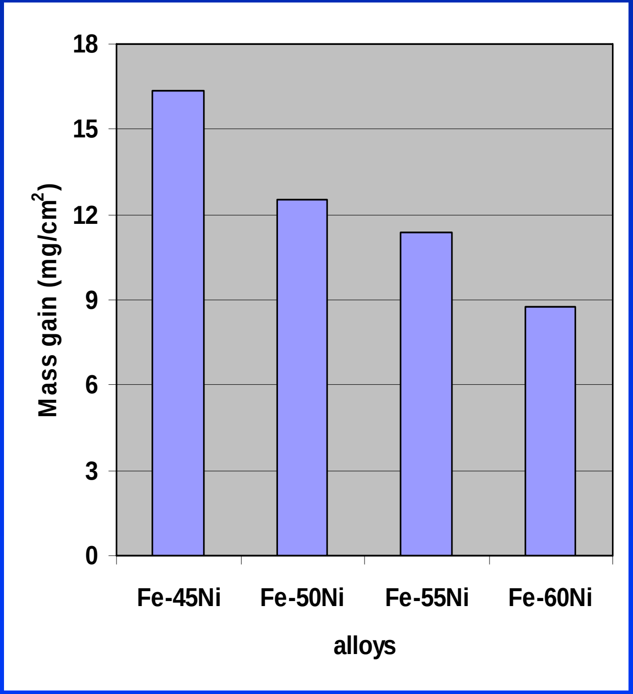
Excellent Match in Thermal Expansion of $Fe_{0.9}Ni_{2.1}O_4$ with the Fe-Ni alloys



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

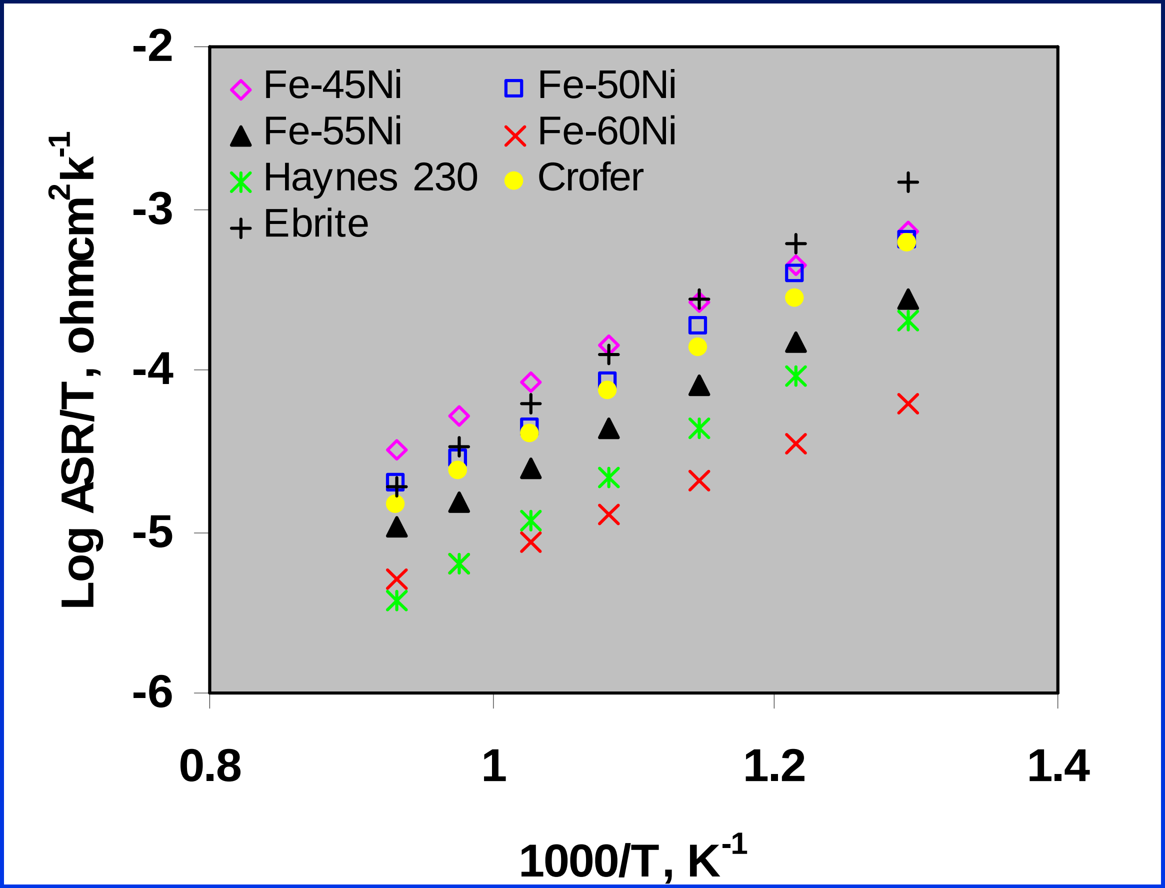
Effect of Ni Content on Oxidation Resistance of the Fe-Ni Binary Alloys in Air 800°C-500h





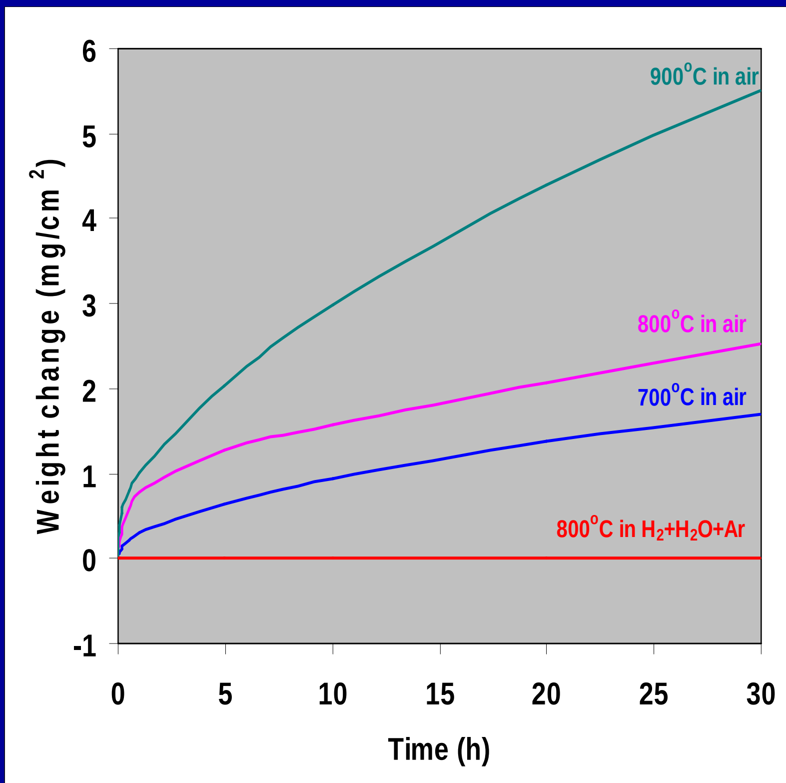
- The mass gain of Fe-Ni alloys decreased with the increase of Ni content in the alloys.
- The oxides scale became thinner with the increase in Ni content.
- The thickness of the surface Fe_2O_3 layer decreased with the increase of Ni content.
- No NiO was formed on Fe-45Ni, while NiO was formed between the spinel and substrate on Fe-50Ni, Fe-55Ni and Fe-60Ni. The continuity of the NiO layer on Fe-55Ni and Fe-60Ni was better than on Fe-50Ni.

Comparison of ASR of the Oxide Scale on Fe-Ni Binary Alloys with Other Alloys

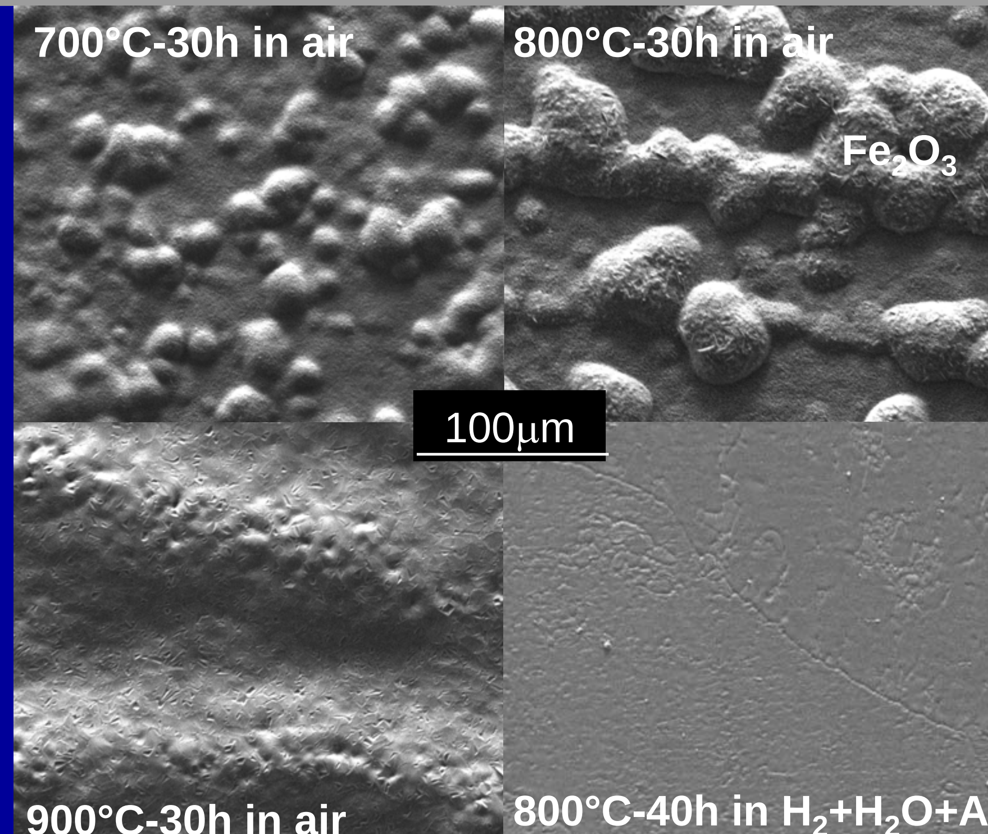


- The ASR of the oxide scale formed on the Fe-Ni alloys after oxidation at 800°C for 500h in air decreased with the increase of Ni content.
- The ASR of the oxide scale formed on the Fe-Ni alloys was comparable to that formed on Ebrite, Crofer and Haynes 230.

Effect of Temperature and Atmosphere on Oxidation Behavior of Fe-50Ni-0.05Y



TGA Data



SEM Surface Morphologies

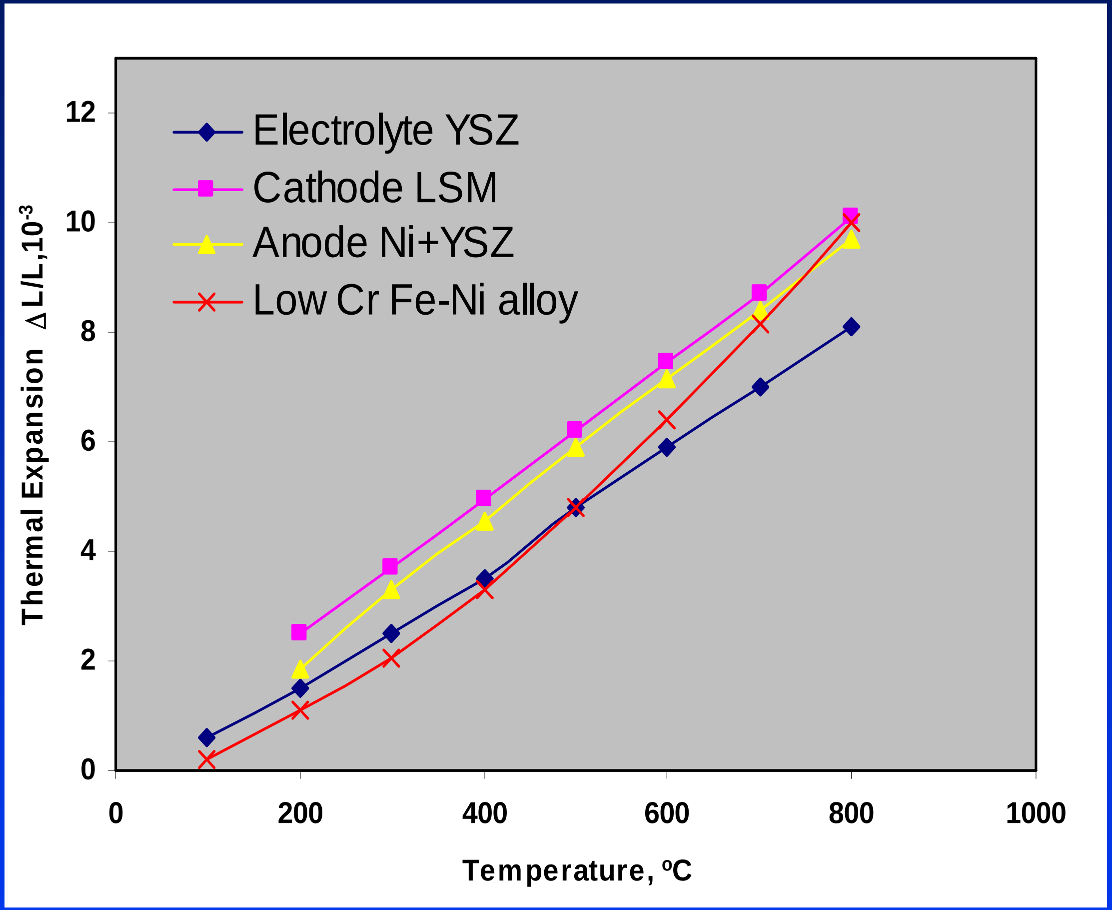
- The mass gain in the cathode environment (air) increased with the increase of oxidation temperature. The surface oxide nodules increased in size with the increase in oxidation temperature.
- No weight change was noticed in anode environment ($Ar+H_2+H_2O$).

Binary Fe-Ni Alloys:
Identifying the Critical Issues

Low-Cr Fe-Ni Alloy Development:
Approach to Form the Desired Double-Layer Oxide Structure

CTE of the New Low Cr Fe-Ni Based Alloy+

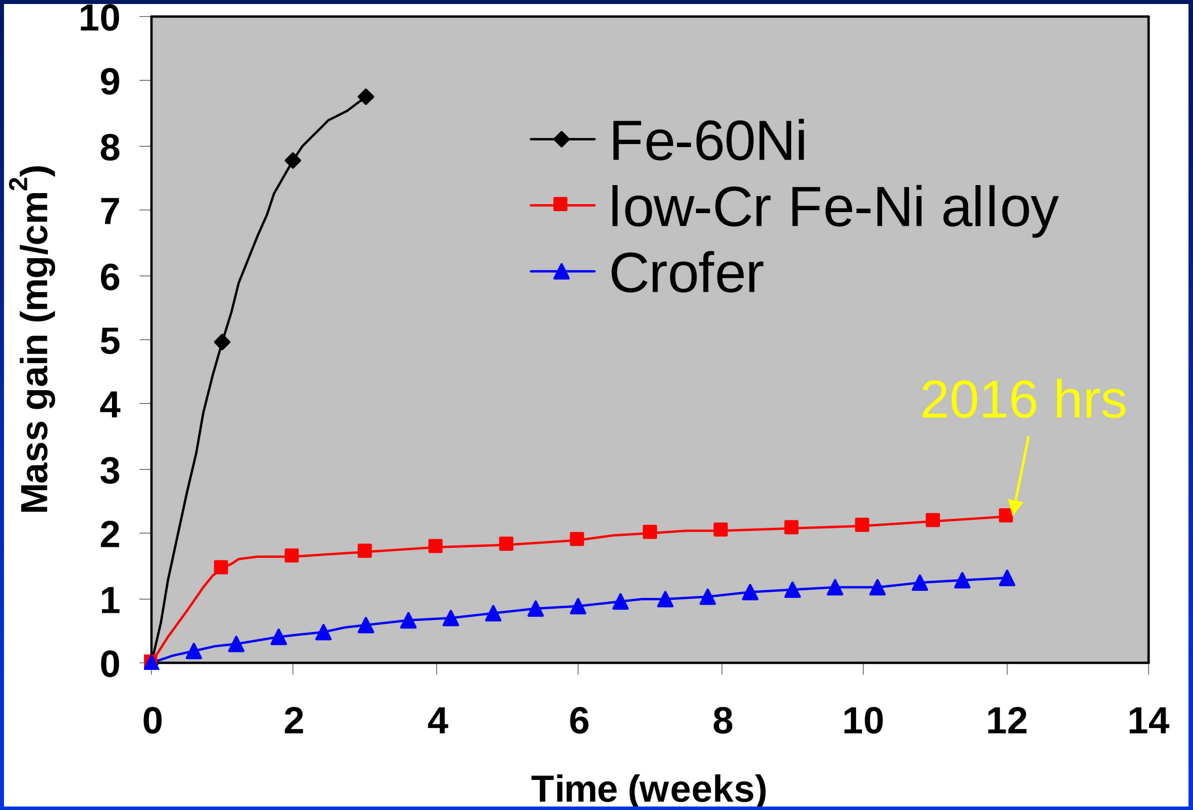
- The formation of continuous, modified Cr_2O_3 inner-layer underneath the spinel out-layer is proposed to enhance the oxidation resistance of the Fe-Ni alloys.
- The CTE of the Fe-Ni alloys increases as Cr content increases.
- The thermal expansion behavior of the new low Cr (6wt.%) Fe-Ni based alloy was close to that of other cell components



Thermal Expansion vs. Temperature for the low Cr Fe-Ni Alloy, as Compared to Other Cell Components

+ The exact alloy composition – proprietary information

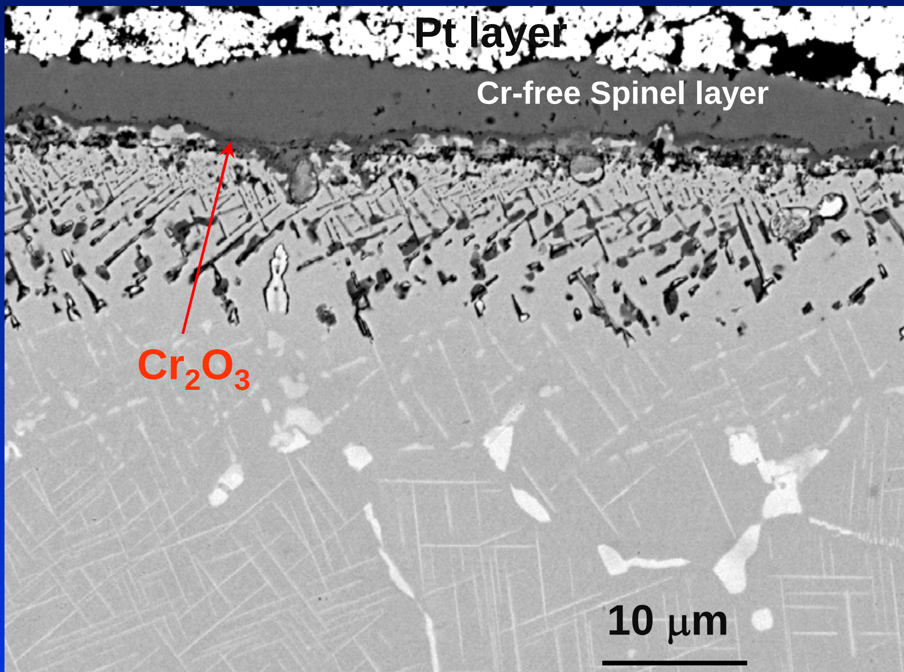
Isothermal Oxidation Kinetics of the Low-Cr Fe-Ni Based Alloy in Air at 800°C



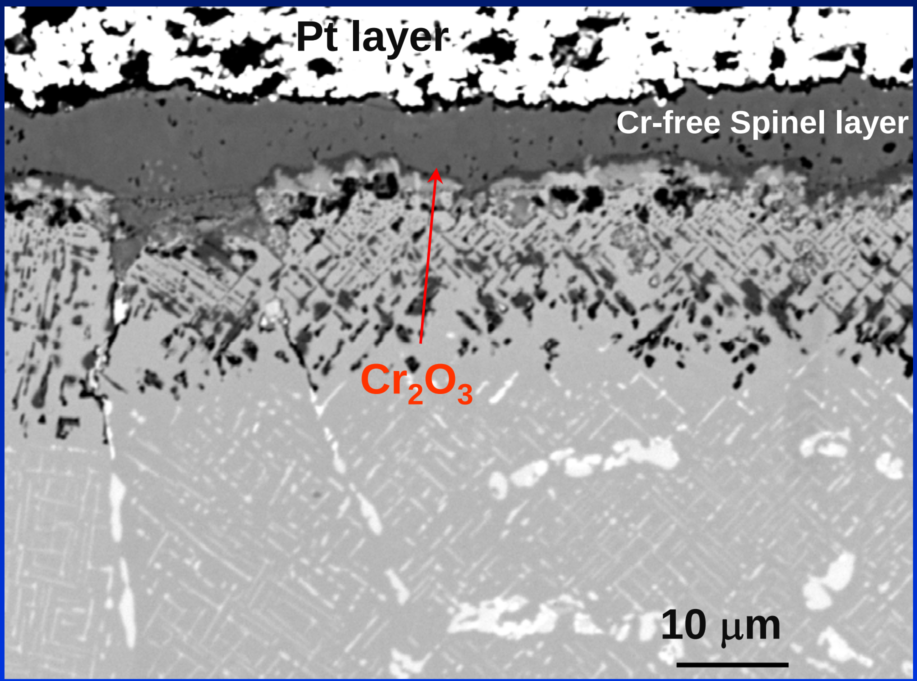
- The newly-developed low-Cr Fe-Ni alloy showed significantly improved oxidation resistance compared to the binary Fe-Ni alloys
- After the 1st-week exposure, the oxidation rate of the new alloy was similar to that of Crofer.
- Large weight gain in the 1st week for the low-Cr Fe-Ni alloy was due to the *in-situ* formation of a Cr-free spinel layer.

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

3 weeks

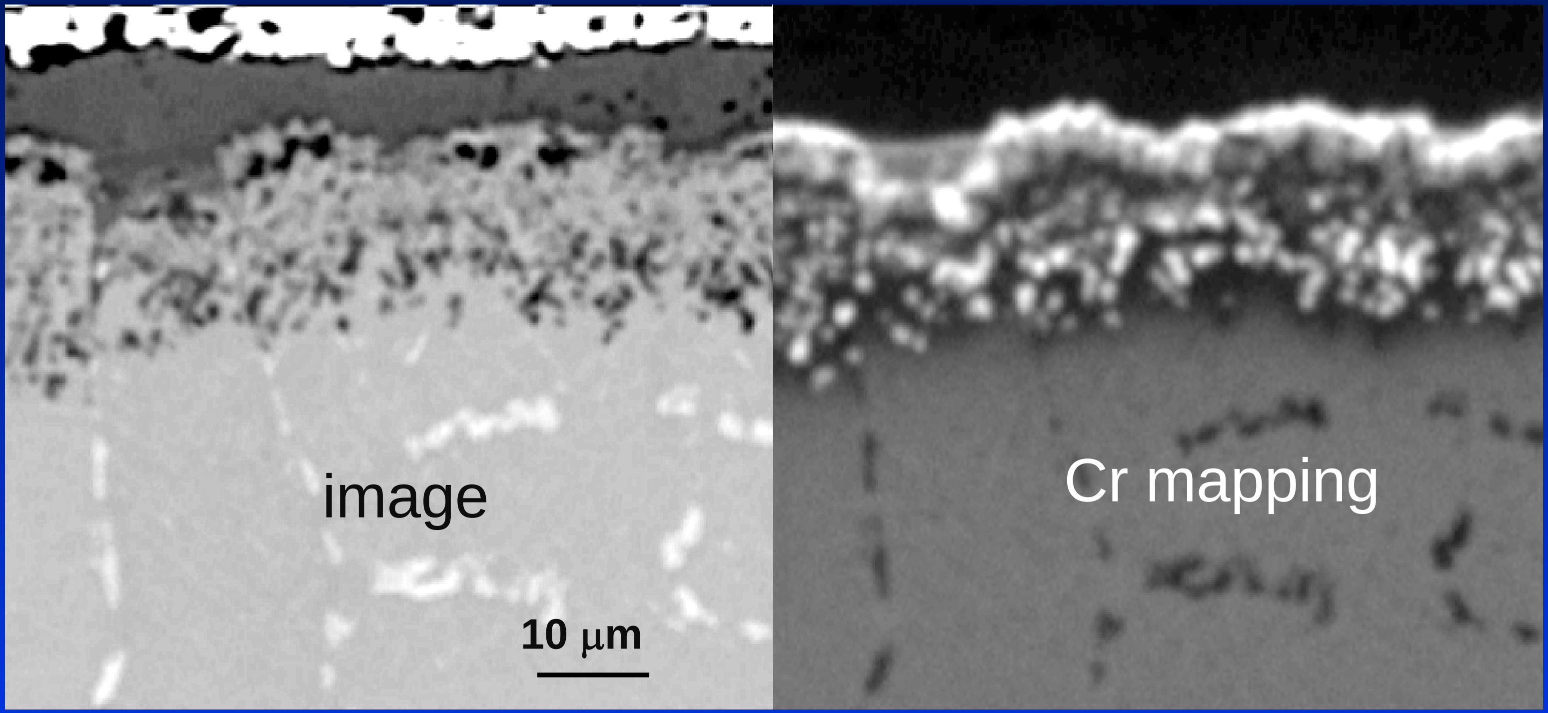


12 weeks



- **The oxide scale formed on this alloy consisted of Cr-free spinel outer layer and chromia inner layer**
- **An internal oxidation zone with mainly Cr_2O_3 was observed underneath the chromia inner layer**

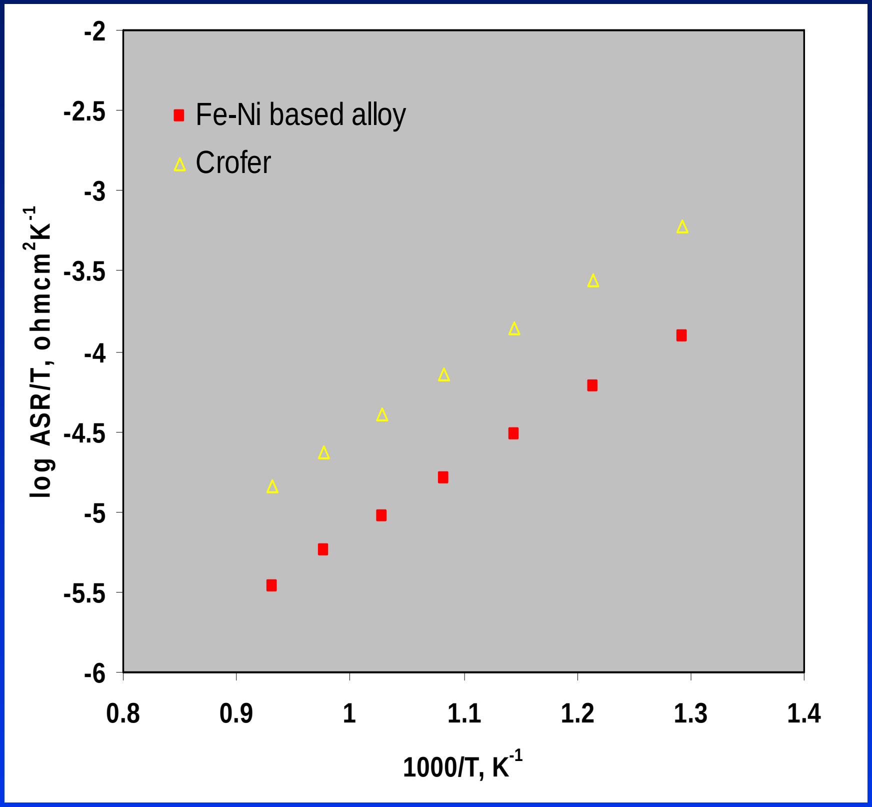
EPMA Result of the Low-Cr Fe-Ni Alloy after Oxidation for 12 weeks at 800°C in Air



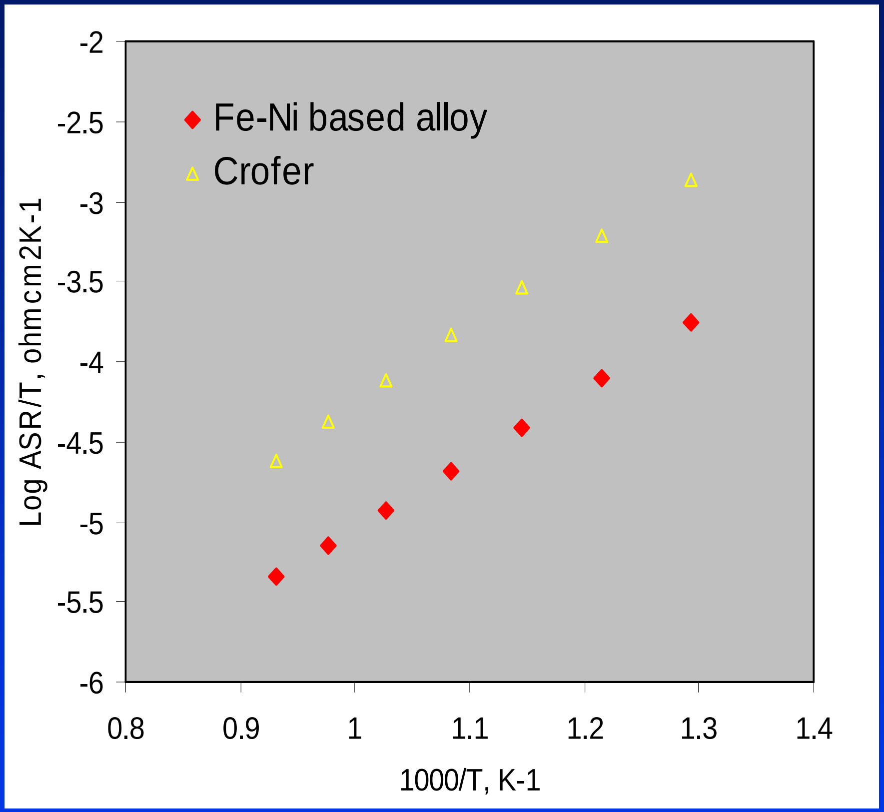
- **The spinel outer layer was essentially Cr-free**
- **The Cr_2O_3 inner layer is continuous**

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

3 weeks



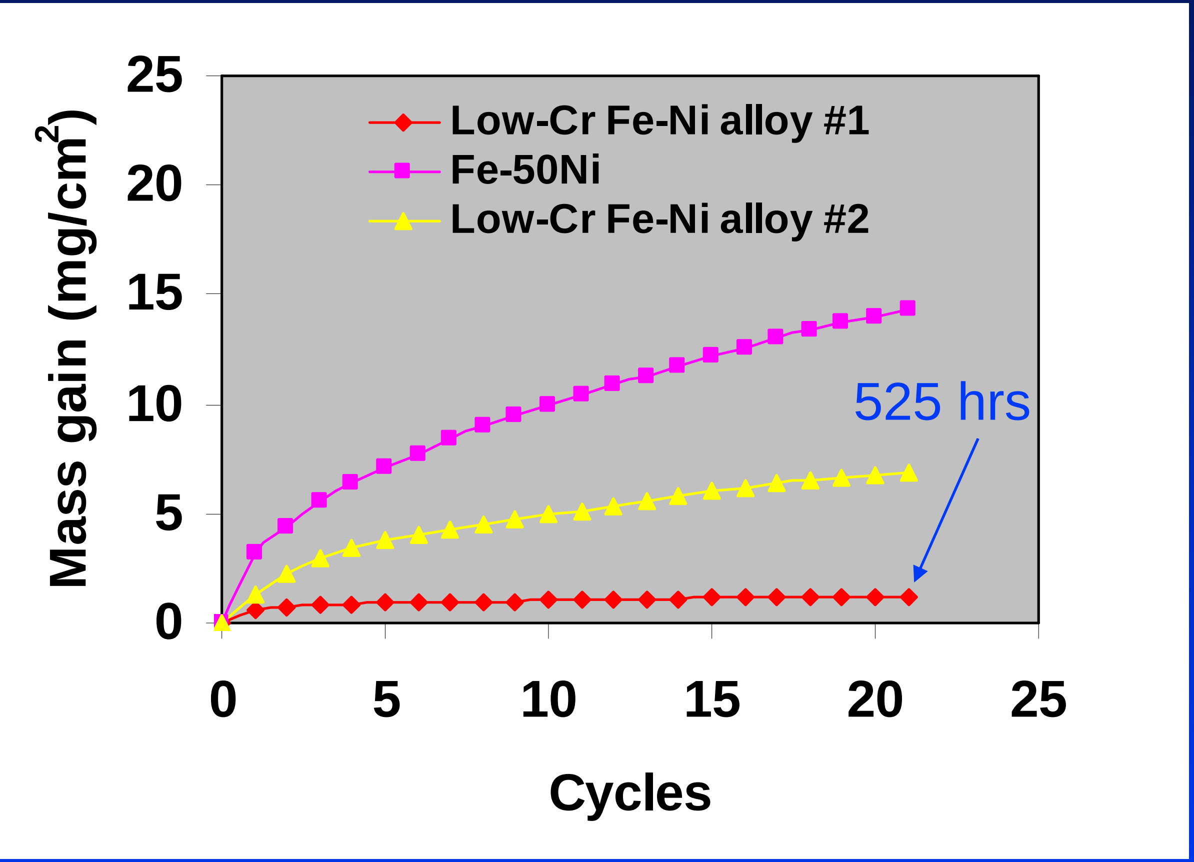
12 weeks



- **The ASR of the oxide scale on the low-Cr Fe-Ni alloy after oxidation for 12 weeks was almost the same as that for 3 weeks**
- **The ASR of the oxide scale on Fe-Ni based alloy** was **lower than that on Crofer**

Cyclic Oxidation of Low-Cr Fe-Ni Based Alloys at 800°C in Air

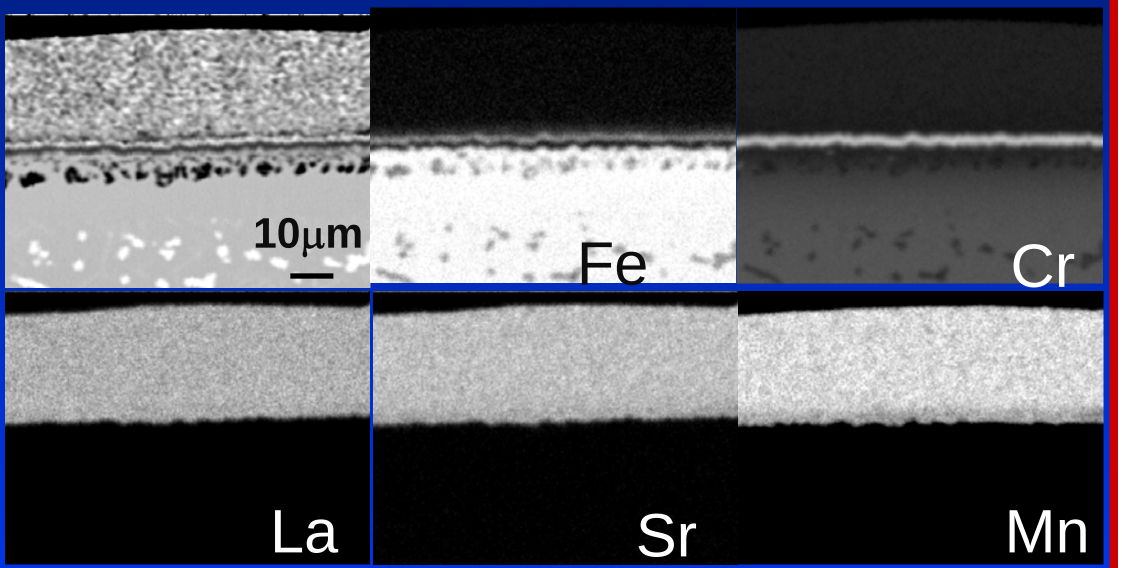
Each cycle consisted of holding at 800°C for 25 hours in air, followed by cooling to room temperature in air

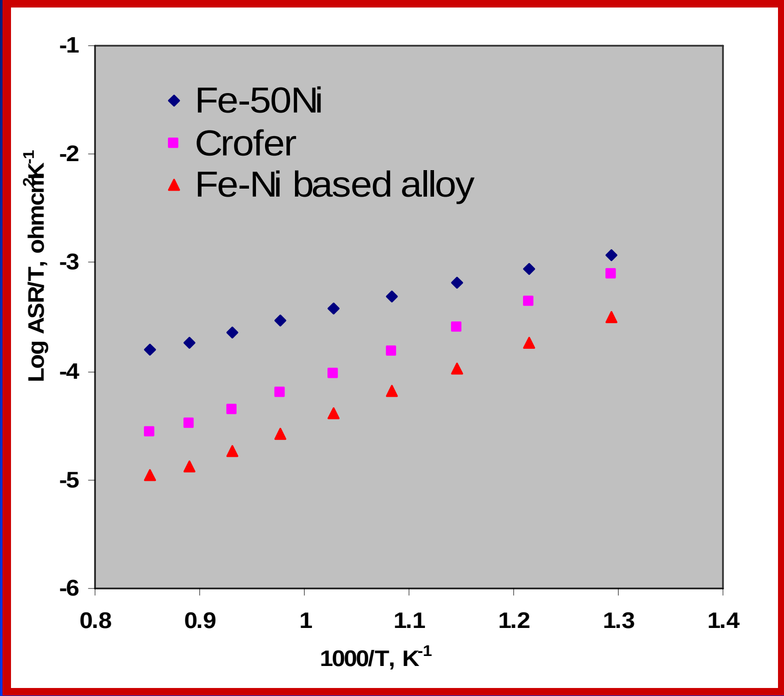


- The mass gain of the optimized low-Cr Fe-Ni based alloy (#1) increased slightly with cycling after the first cycle
- No spallation was observed for all the alloys, consistent with the CTE data

Compatibility of the New Alloy with Cathode (LSM)

The alloy/cathode couples were oxidized for 300 hours at 900°C in air





Cross-section of the low Cr Fe-Ni based alloy with LSM

ASR of the low Cr Fe-Ni based alloy coated LSM

- **Negligible interaction between the oxide scale and LSM**
- **Lower ASR for the low-Cr Fe-Ni alloy than that for Crofer**

Summary

- **CTE (√)**

The CTE of the binary and low Cr Fe-Ni alloys is close to that of other cell components.

- **ASR (√)**

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

- **Oxidation Resistance (√)**

While the oxidation resistance of the binary Fe-Ni alloys is not satisfactory, effective alloying additions have been identified to overcome this problem.

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

Current/Future Work

- **Current Work: On-going Phase I Study**
  - **Alloy Modification to Improve Oxidation Resistance and CTE**
  - **Oxidation Tests in Simulated Anode Environment as well as in Air with Different Water Vapor Levels**
  - **In-depth Study of Electrical Conduction Mechanism in $NiFe_2O_4$ spinel**
  - **Detailed Study of Alloy/Cathode Interaction/Compatibility**
  - **Cr Volatility Measurement at PNNL**
- **Future Work: Proposed Phase II Study**
  - **Further Optimization of Alloy Compositions**
  - **Scale-up of Alloy Production (in Collaboration with Some Commercial Alloy Producers)**
  - **Cell/Stack Testing with the New Interconnect Alloy (In-house, National Laboratories, SECA Industrial Teams)**
  - **Evaluation of Other Properties (Forming, Tensile, Creep, etc.)**

Acknowledgements

- This research was sponsored by the DOE SECA Core Technology Program (DOE Award #DE-FC26-04NT42223). The authors wish to thank Dr. Lane Wilson at NETL for helpful discussions regarding this work.
- Additional support was provided by the Center for Manufacturing Research, Tennessee Technological University.