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

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

- Currently, the interconnect materials for intermediate temperature SOFC are mainly 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(VI) species under the SOFC operating environments:

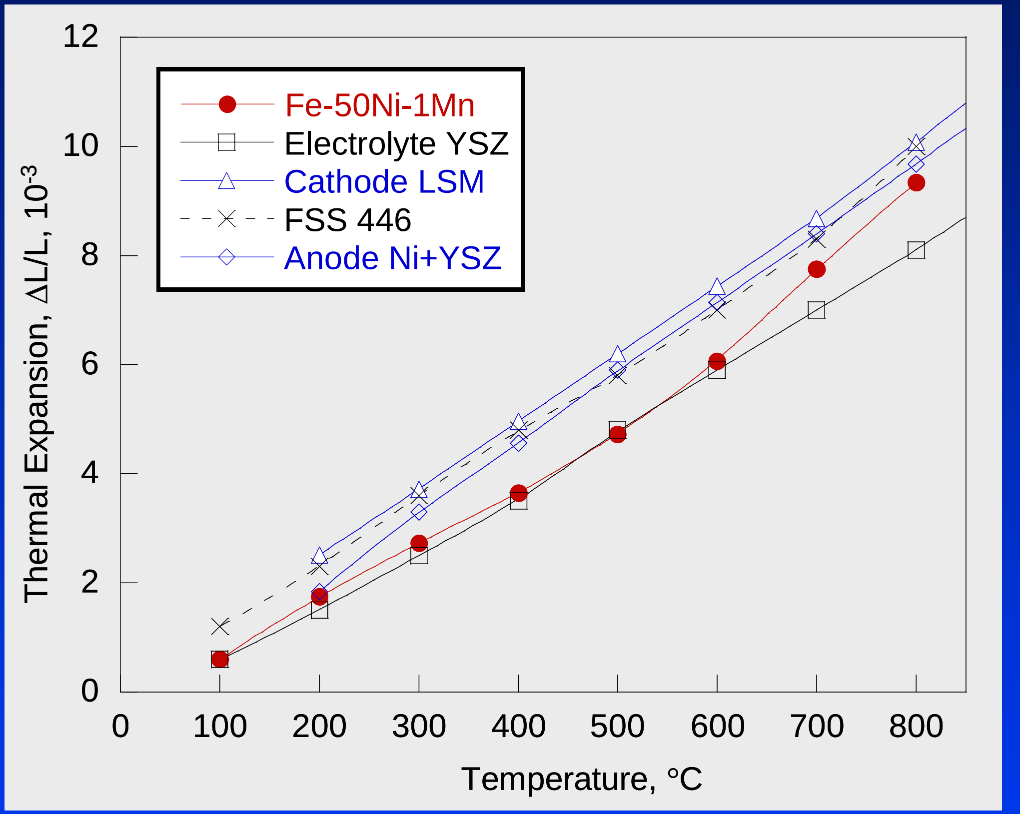
$$2Cr_2O_3(s) + 3O_2(g) \leftrightarrow 4CrO_3(g)$$
$$2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \leftrightarrow 4CrO_2(OH)_2(g)$$
$$Cr_2O_3(s) + O_2(g) + H_2O(g) \leftrightarrow 2CrO_2OH(g)$$

The Cr species might migrate to and thus poison the cathode, resulting in SOFC performance degradation.

Cr-free or low Cr alloys might completely resolve the Cr poisoning issue in SOFC stacks.

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

- Fe-Ni alloys with about 50 wt. %Ni exhibit coefficient of thermal expansion (CTE) 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 alloys might be tailored via alloy design



Thermal Expansion vs. Temperature for the Fe-50Ni-1Mn Alloy (wt.%), as Compared to Other Cell Components

This SECA project is a collaborative effort between TTU, ORNL, and UMR

- **Alloy Design (TTU and ORNL)**

  Physical metallurgy principles are being utilized to design and develop a new generation of Fe-Ni based alloys with suitable performance

- **Electrical Conductivity of $NiFe_2O_4$ Spinel (TTU and UMR)**

  Electrical conductivity and electrical conduction mechanism of $NiFe_2O_4$-base spinel thermally grown on the Fe-Ni alloys are being evaluated

- **Characterization (TTU, ORNL, UMR)**
  - Isothermal oxidation kinetics and cyclic oxidation resistance of the developed alloys
  - The ASR (area specific resistance) of the oxide scales
  - Compatibility of the developed alloys with SOFC cathode materials

Alloy Design Strategies

- **CTE Match with Other Cell Components**

  Fe, Co, Ni, Mo, Nb, and Ti contents will be controlled to maintain the CTE values of the new Fe-Ni alloys at the desired level.

- **Electrical Resistance of the Oxide Scales**

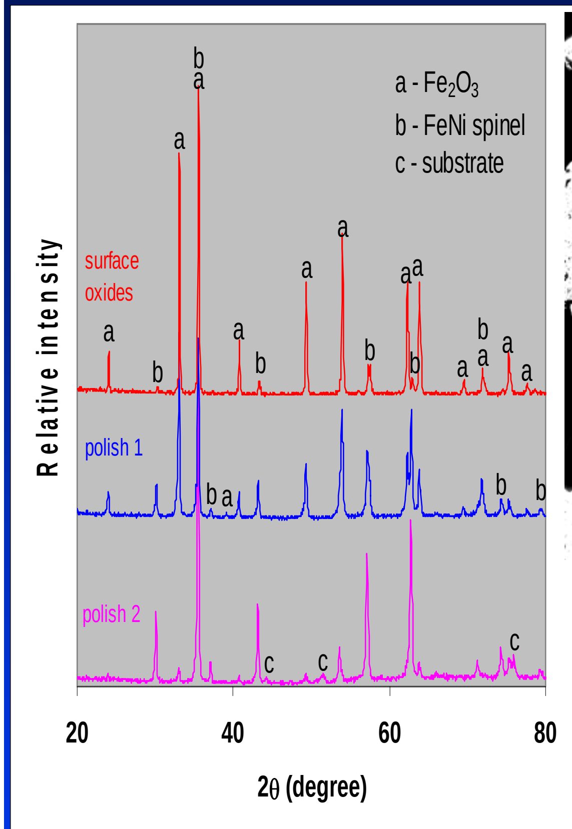
  In addition to control the Fe-Ni ratio, other transition metals will be added to increase the electrical conductivity of the outer-layer $NiFe_2O_4$ spinel.

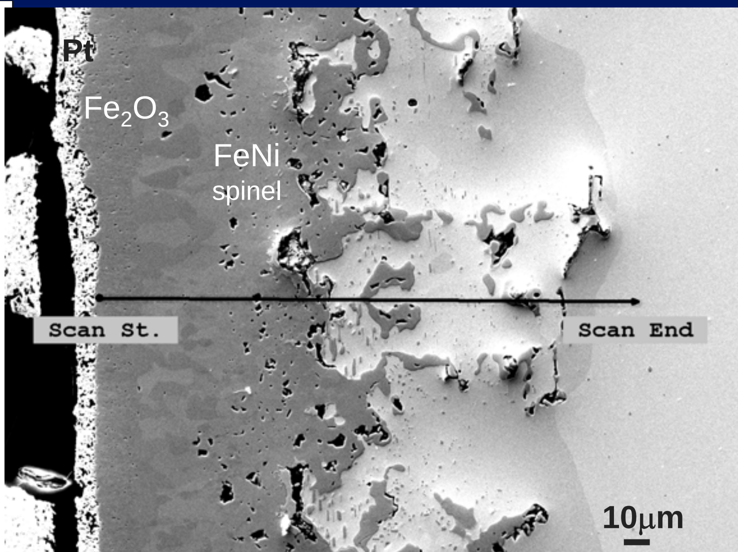
- **Oxidation resistance of Fe-Ni alloys**

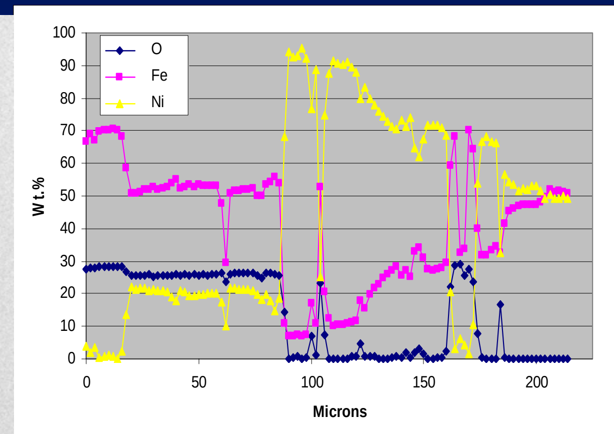
  An inner layer of dense, protective, and electrically conductive oxide (e.g. NiO, Cr_2O_3) will be formed after rapid local surface depletion of Fe during initial oxidation.

Schematic of the Desirable Double-Layer Oxide Structure

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





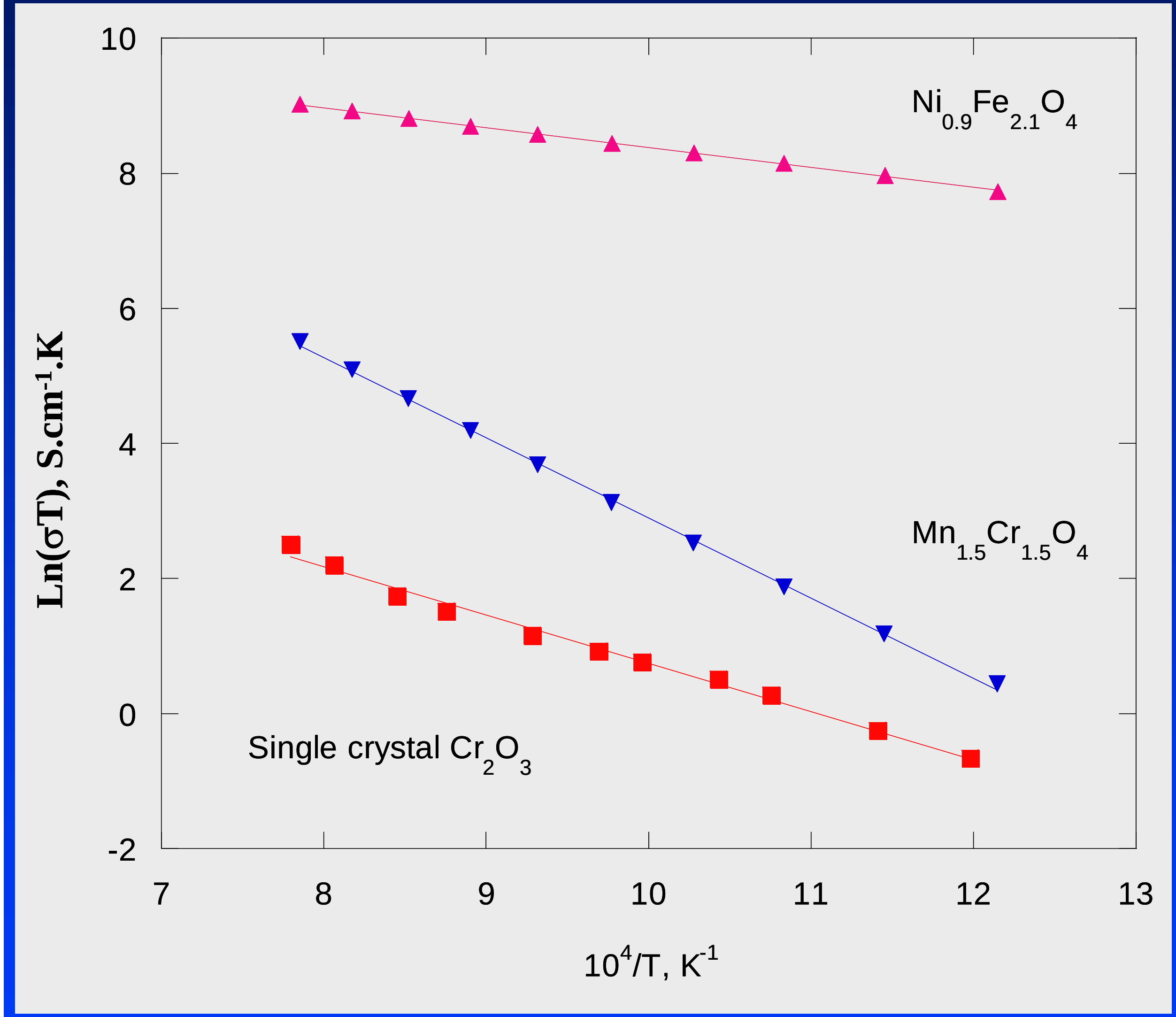


XRD patterns, cross-section, and electron-probe micro-analysis (EPMA) results of Fe-50Ni-0.05Y after oxidation for 500h in air at 800°C

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

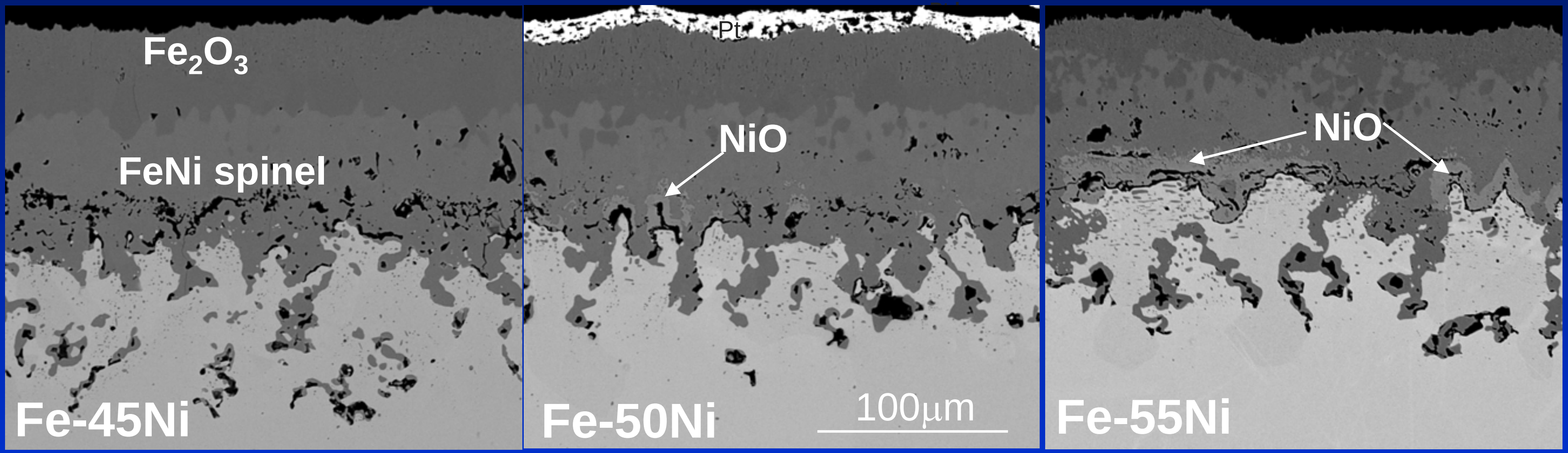


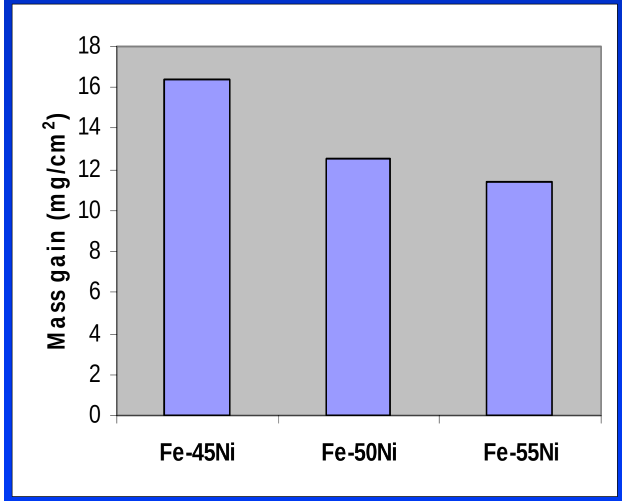
Dense pellets of $Ni_{0.9}Fe_{2.1}O_4$ and $Mn_{1.5}Cr_{1.5}O_4$ were used for electrical conductivity measurement:

- ✓ **$Ni_{0.9}Fe_{2.1}O_4$ 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)**

Effect of Ni Content on Oxidation Resistance of the Fe-Ni alloys

Cross-section of the Fe-Ni alloys with different Ni contents after oxidation for 500h at 800°C in air

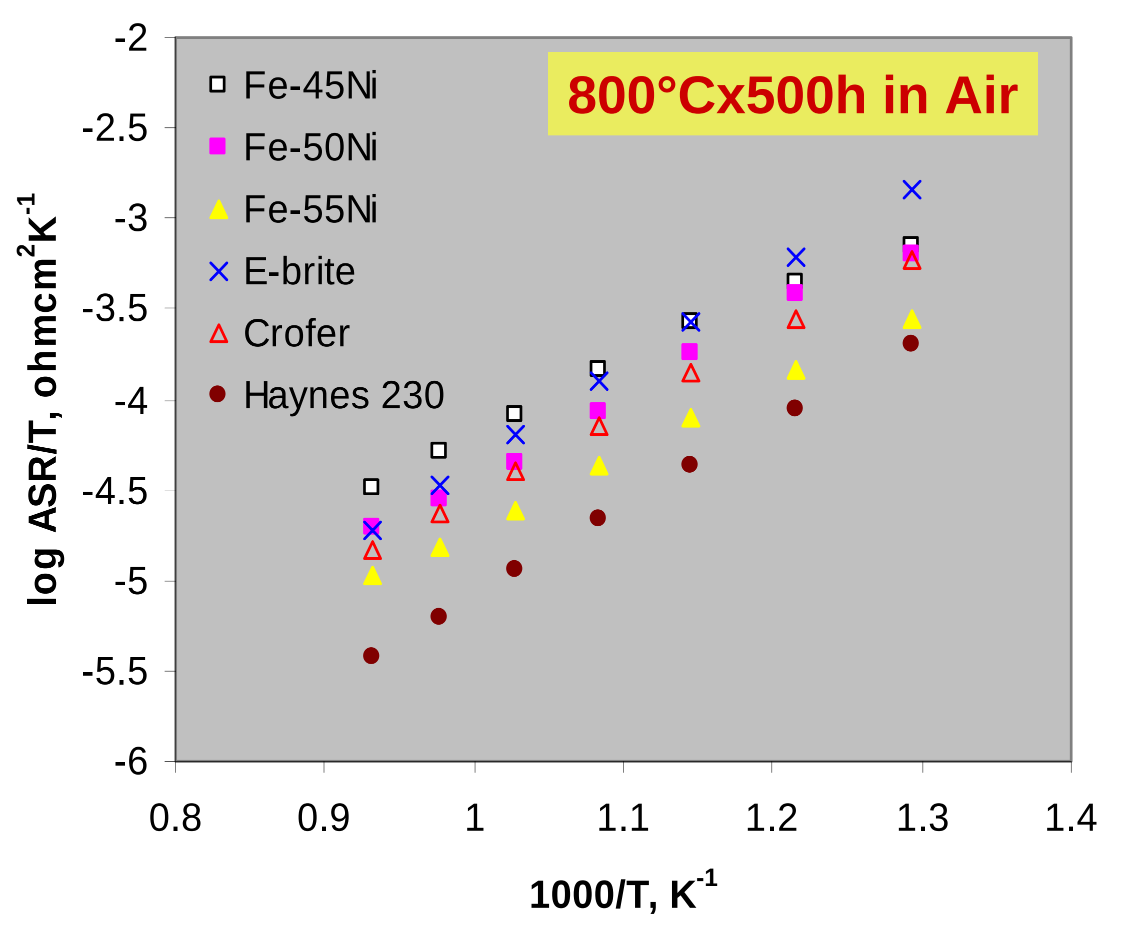




Mass Gain after Oxidation

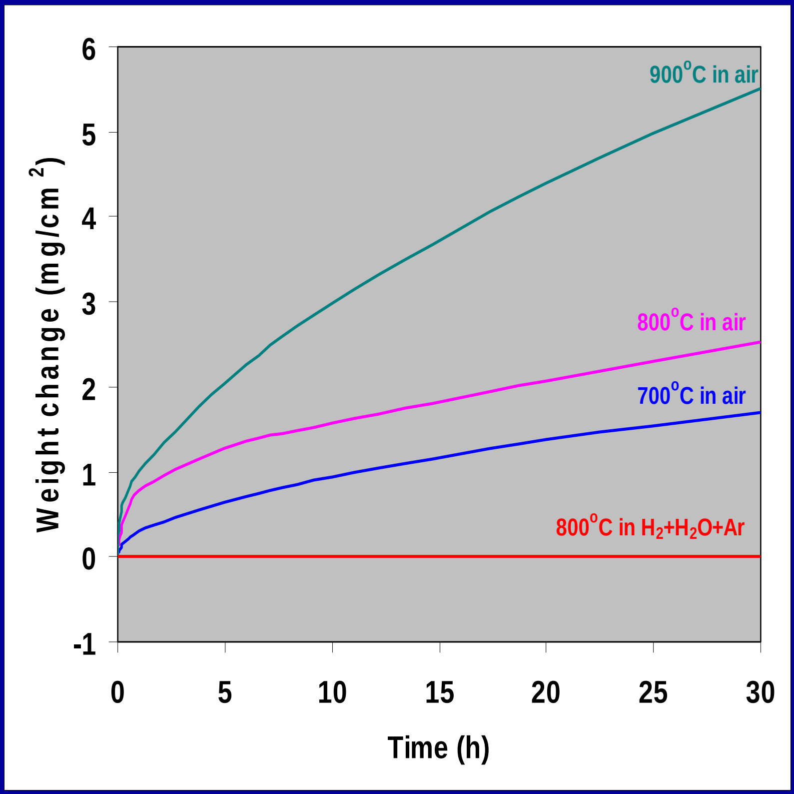
- **The mass gain of Fe-Ni alloys decreased with the increase of Ni content in the alloys.**
- **The oxides scale became thinner with the increase in Ni content.**
- **The thickness of Fe_2O_3 layer decreased with the increase of Ni content.**
- **No NiO was formed on Fe-45Ni, while NiO was formed between the spinel and substrate on both Fe-50Ni and Fe-55Ni. The continuity of the NiO layer on Fe-55Ni was better than on Fe-50Ni, but not yet good enough**

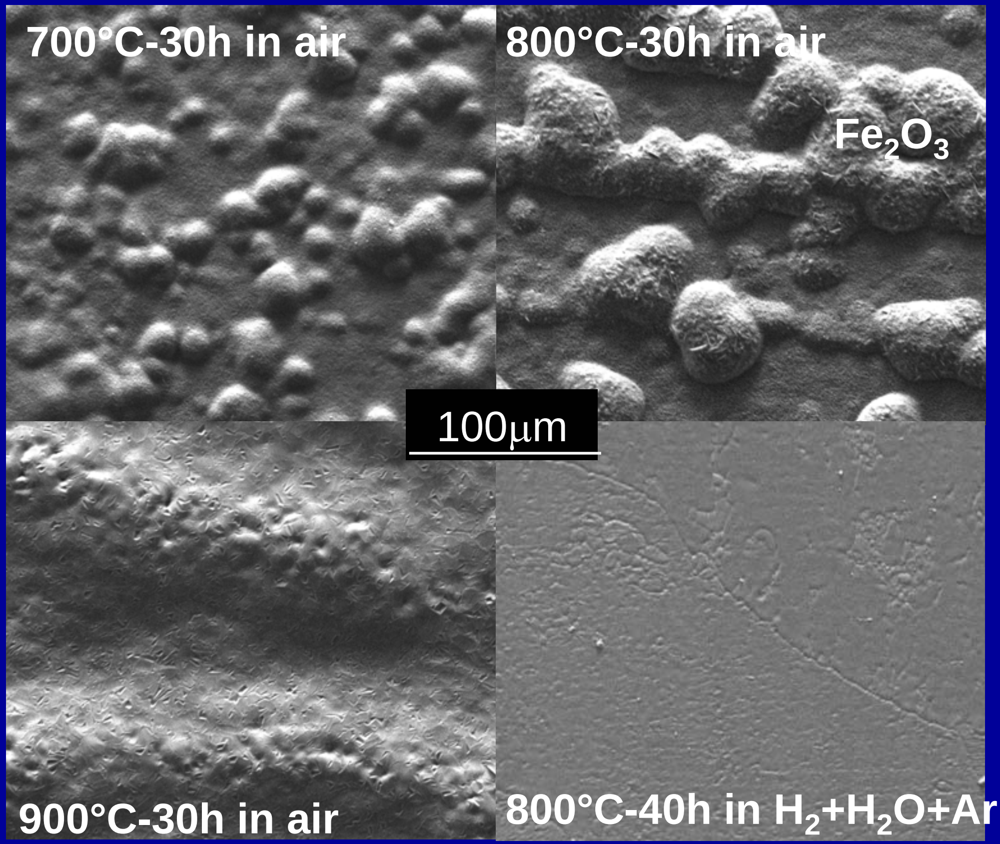
Comparison of ASR of the Oxide Scale Formed on Fe-Ni Alloys with Other Alloys



- **The ASR of the oxide scale formed on 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 Fe-Ni alloys was comparable to that of Ebrite and Crofer, and slightly higher than that of Haynes 230**

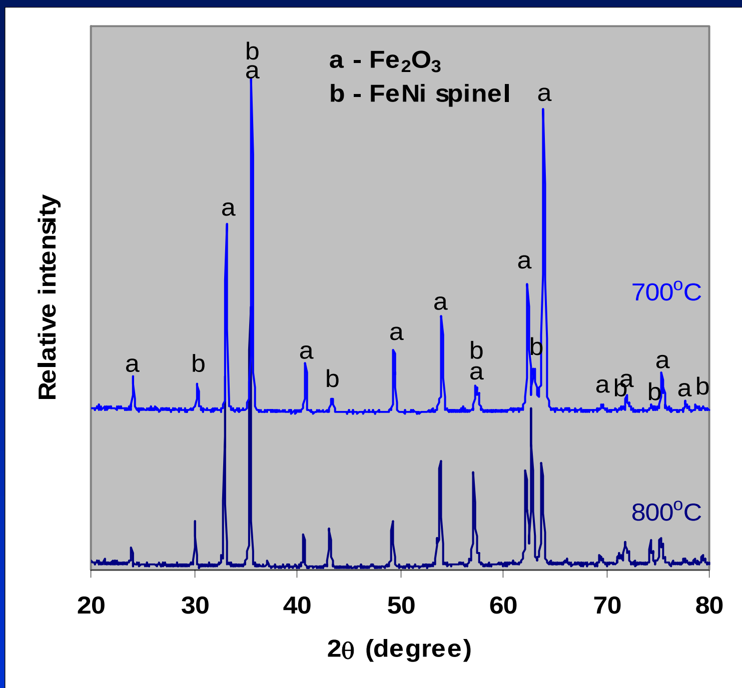
Effect of Temperature and Atmosphere on Oxidation Behavior of Fe-50Ni-0.05Y



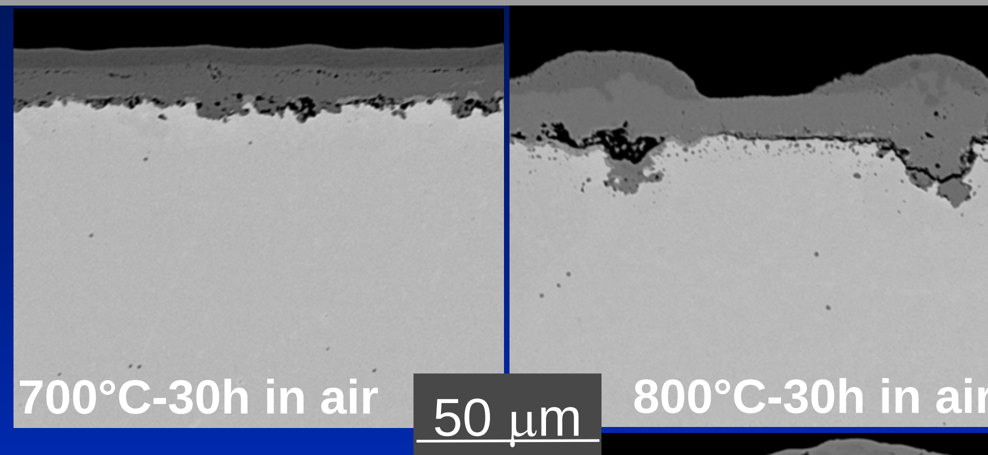


- The mass gain in the cathode environment (air) increased with the increase of oxidation temperature. The surface oxide nodules increased in size with the increase in oxidation temperature.
- No weight change was noticed in anode environment (Ar+H_2+H_2O).

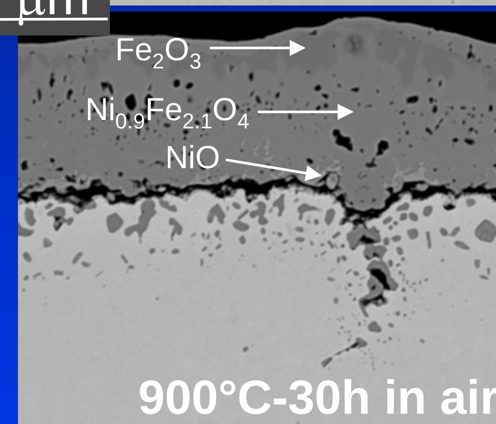
Oxide Scale Structures after Isothermal Oxidation



XRD of Fe-50Ni after oxidation for 30h in air at 700°C and 800°C



Cross-sections of Fe-50Ni-0.05Y after oxidation



The oxide scale structures formed on Fe-50Ni-0.05Y:

- 700°C: Fe_2O_3 top layer, FeNi spinel layer and a thin NiO layer.
- 800°C: Fe_2O_3 top layer, FeNi spinel layer and a thin NiO layer.
- 900°C: Fe_2O_3 layer inserted in the FeNi spinel layer with a thin NiO layer near the substrate

Future Work

- **Electrical Conductivity of $NiFe_2O_4$ Spinel**

  The effects of stoichiometry, transition metal addition, and reactive element doping on the electrical conductivity of the $NiFe_2O_4$ spinel will be characterized.

- **Oxidation Resistance**

  Alloy design of the Fe-Ni system will be continued to enhance their oxidation resistance in the SOFC operating environments.

- **Coefficient of Thermal Expansion (CTE)**

  The CTE of the development alloys will be determined before and after oxidation.

- **Compatibility with Other SOFC Components**

  The compatibility of the Fe-Ni alloys with cathode material will be assessed.

Concluding Remarks

- **ASR (√)**

The ASR of the oxide scales formed on the Fe-Ni alloys is comparable to that of current SOFC interconnect alloys.

- **CTE (√)**

The CTE of Fe-Ni alloys is low and close to that of other cell components; however, with additional alloying additions, their CTE might be modified.

- **Oxidation Resistance (?)**

The oxidation resistance of these alloys should be improved in order to fulfill the requirements for SOFC interconnect application. This will be the focus area of this project in the near future.