Advanced Alloy Interconnect Development

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Interconnect Development

Objectives:

- Develop cost-effective, optimized materials for intermediate temperature interconnect and its interface applications.
- Identify and understand degradation processes in candidate alloys.

Approach:

- Screen testing of conventional and newly developed alloys (chemical, electrical, mechanical properties, cost).
- Investigation of oxidation/corrosion behavior of alloys and scale stability under SOFC operating conditions.
- Materials development.
  - Surface modification (surface doping, overlay coatings, cladding).
  - Bulk modification or alloy development.
  - Cathode/interconnect interfaces.

Highlights of Achievements

- Developed standardized testing capability for evaluation of SOFC interconnect alloys
- Identified and evaluated suitable candidate alloys using systematic screening techniques.
- Developed conductive oxide coated alloy interconnects for improved stability.
- Evaluated newly developed alloys, including Crofer22 APU and ZMG232.
- Examined oxidation/corrosion behavior of steels and superalloys.

Evaluation of Newly Developed Alloys

FSS	Fe	Cr	C	Mn	Si	Ti	Al	P	S	RE
Crofer22 APU	Bal.	22.0	0.005	0.5	--	0.08	--	0.016	0.002	0.06La
ZMG232	Bal.	22.0	0.02	0.5	0.40	--	0.21			0.04La 0.02Zr

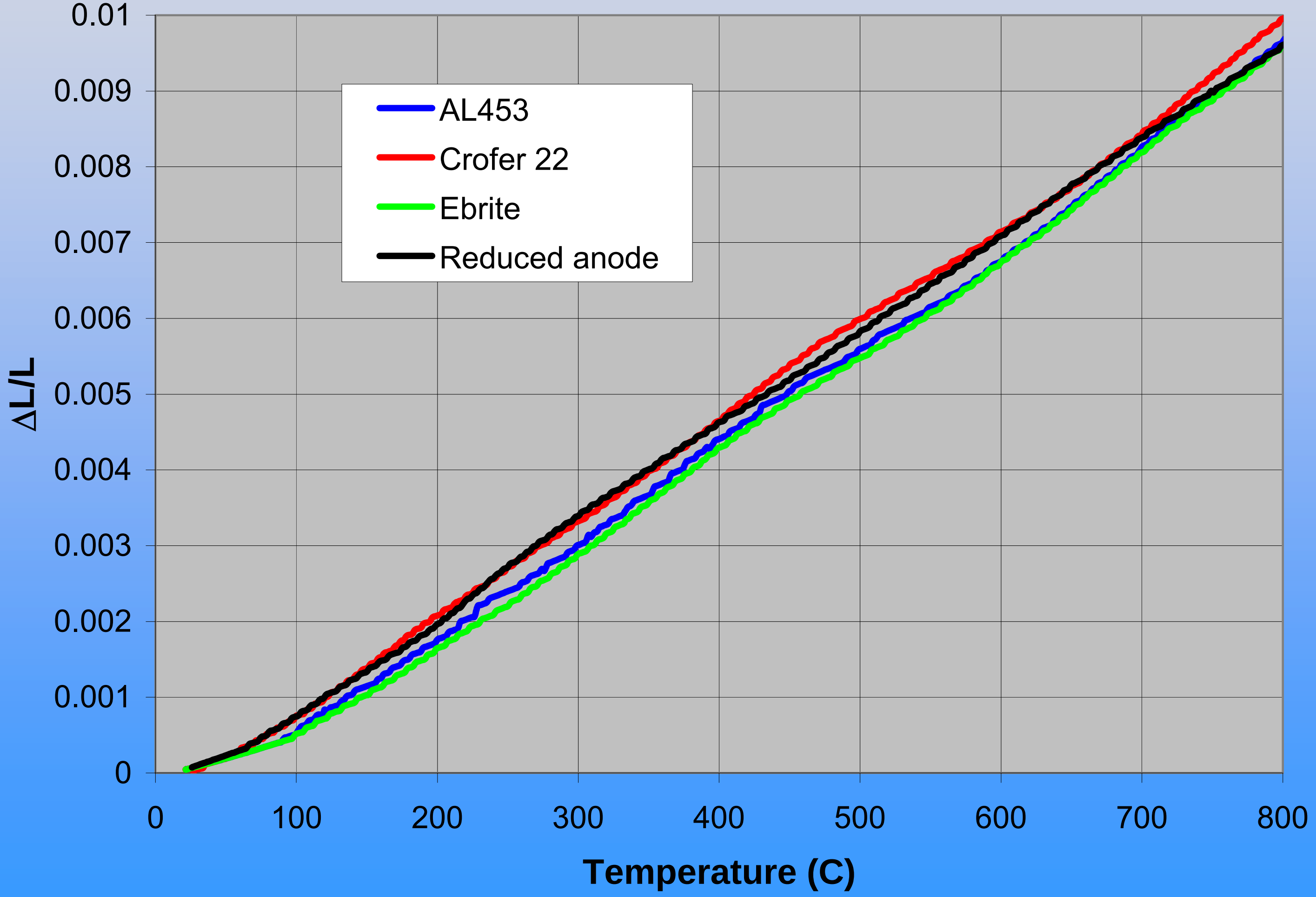
Crofer is a trade mark of ThyssenKrupp; ZMG is a trade mark of Hitachi Metals, Ltd.

Properties relevant to SOFC applications:

- Thermal expansion;
- Scale growth and oxidation resistance;
- Scale electrical conductivity;
- Scale evaporation;
- Compatibility with seals;
- Scale adherence and seal bonding strengths.

Crofer22 APU: Thermal Expansion

Some Fe-Cr ferritic compositions (including Crofer22 APU) demonstrate good CTE matching to the Ni/YSZ anode.

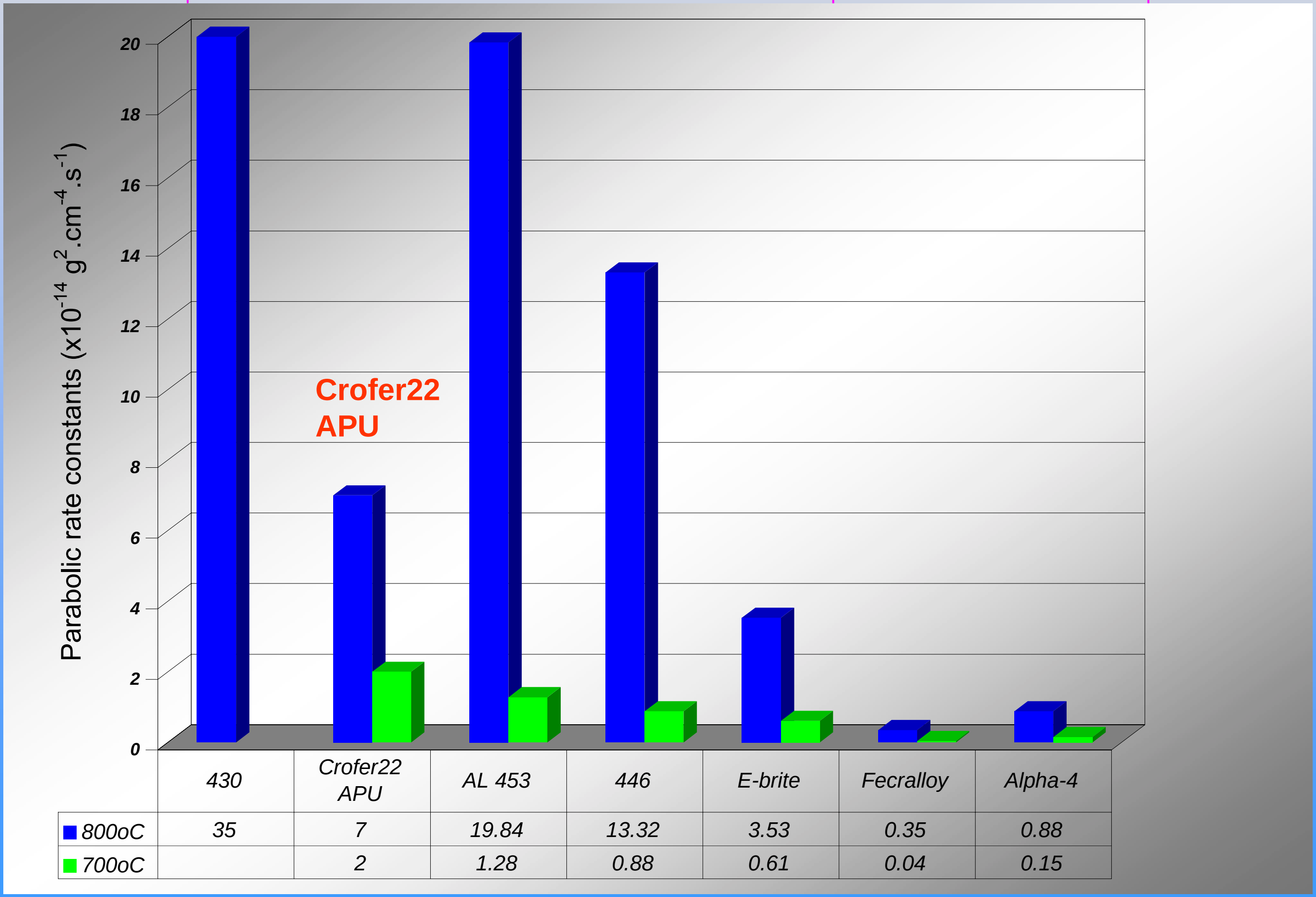


Oxidation Resistance

$$\xi^2 = k_p t = \frac{\kappa_g}{(\chi\rho)^2} t$$

Chromia former

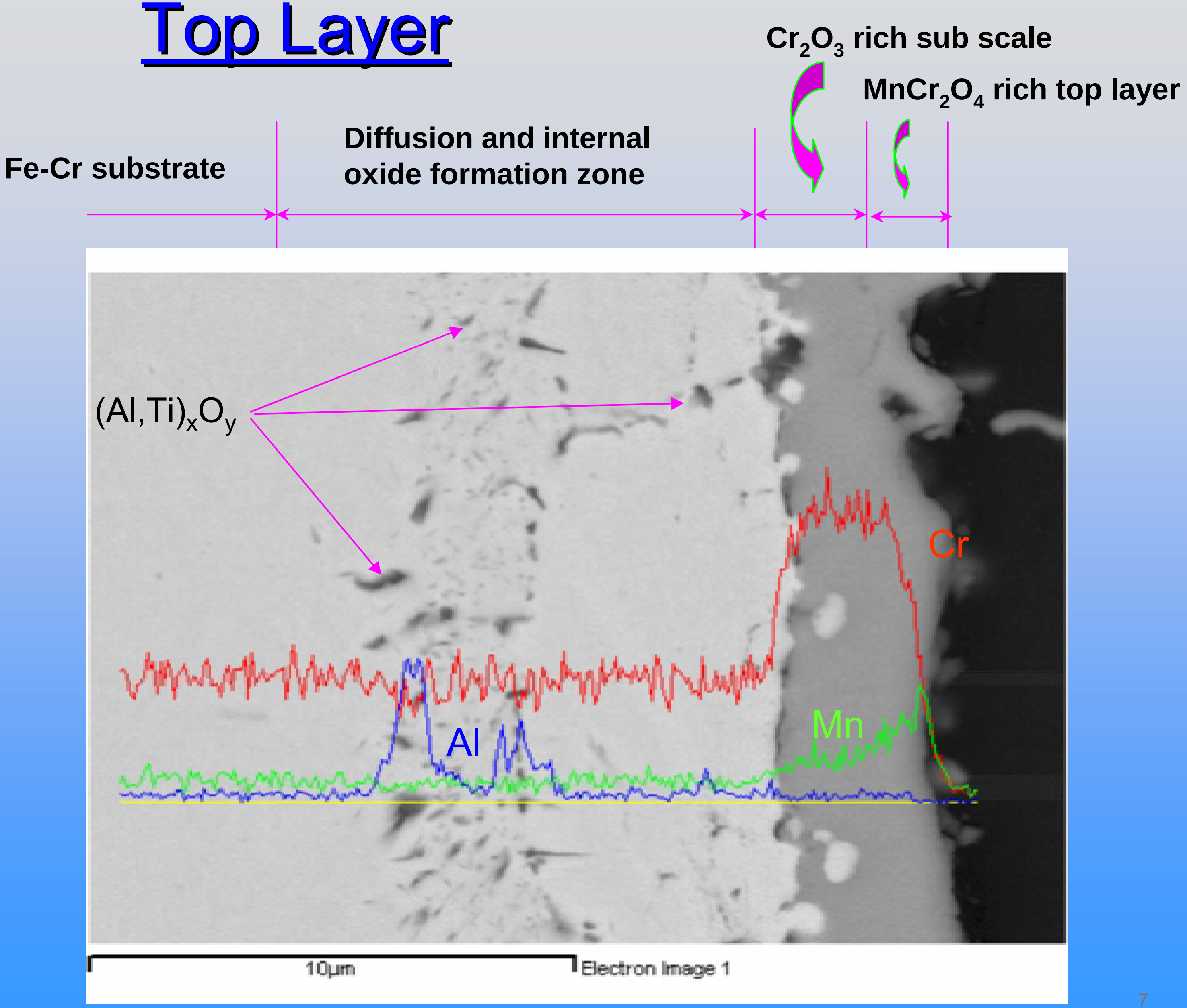
Alumina former



	430	Crofer22 APU	AL 453	446	E-brite	Fecralloy	Alpha-4
🟦 800oC	35	7	19.84	13.32	3.53	0.35	0.88
🟩 700oC		2	1.28	0.88	0.61	0.04	0.15

Formation of (Mn,Cr) Spinel Top Layer

Crofer22 APU was heat treated at 800ºC for 1,200 hours in air



Fe-Cr substrate

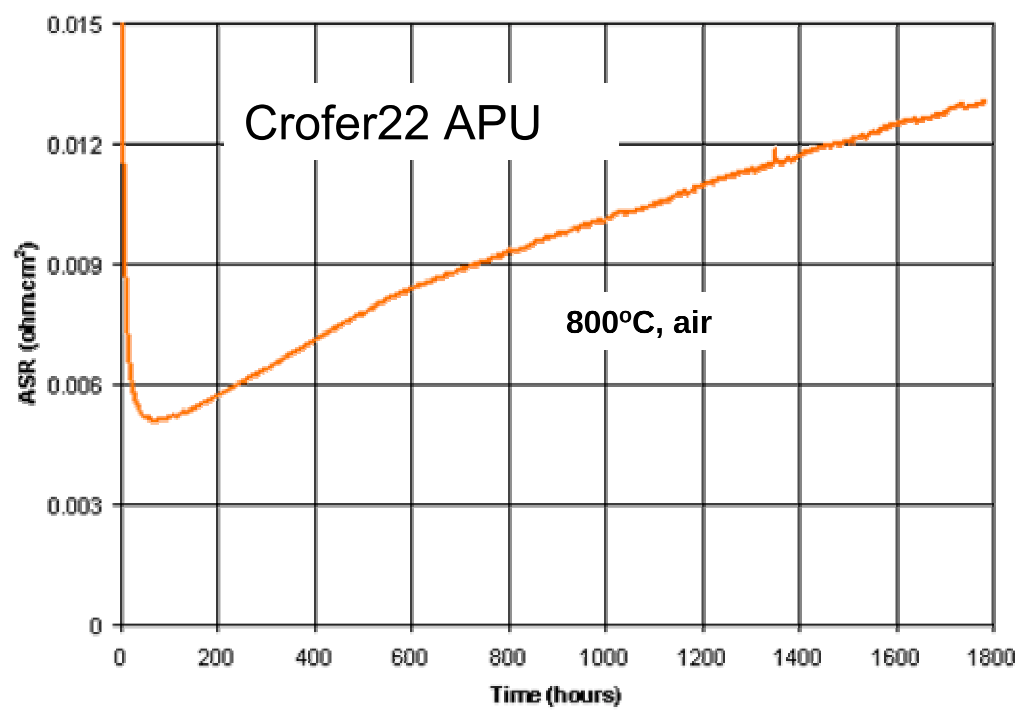
Diffusion and internal oxide formation zone

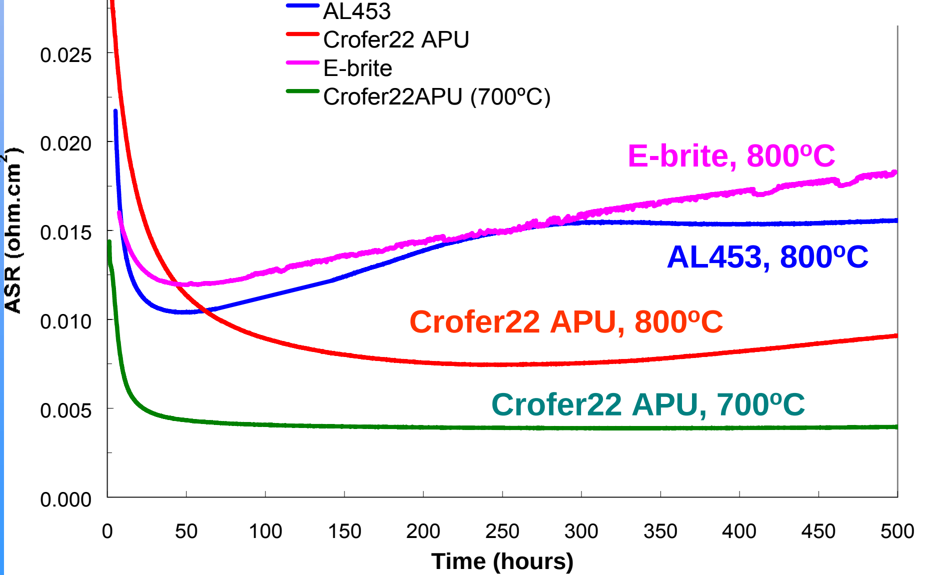
Cr_2O_3 rich sub scale

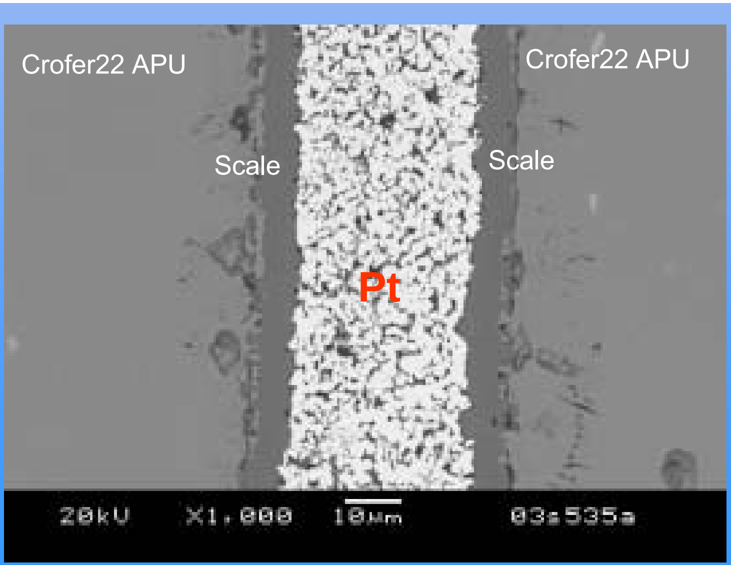
$MnCr_2O_4$ rich top layer

Scale Electrical Conductivity

Extrapolation of the 2,000 h test gives an ASR of about 200 $m\Omega.cm^2$ after 40,000 h.



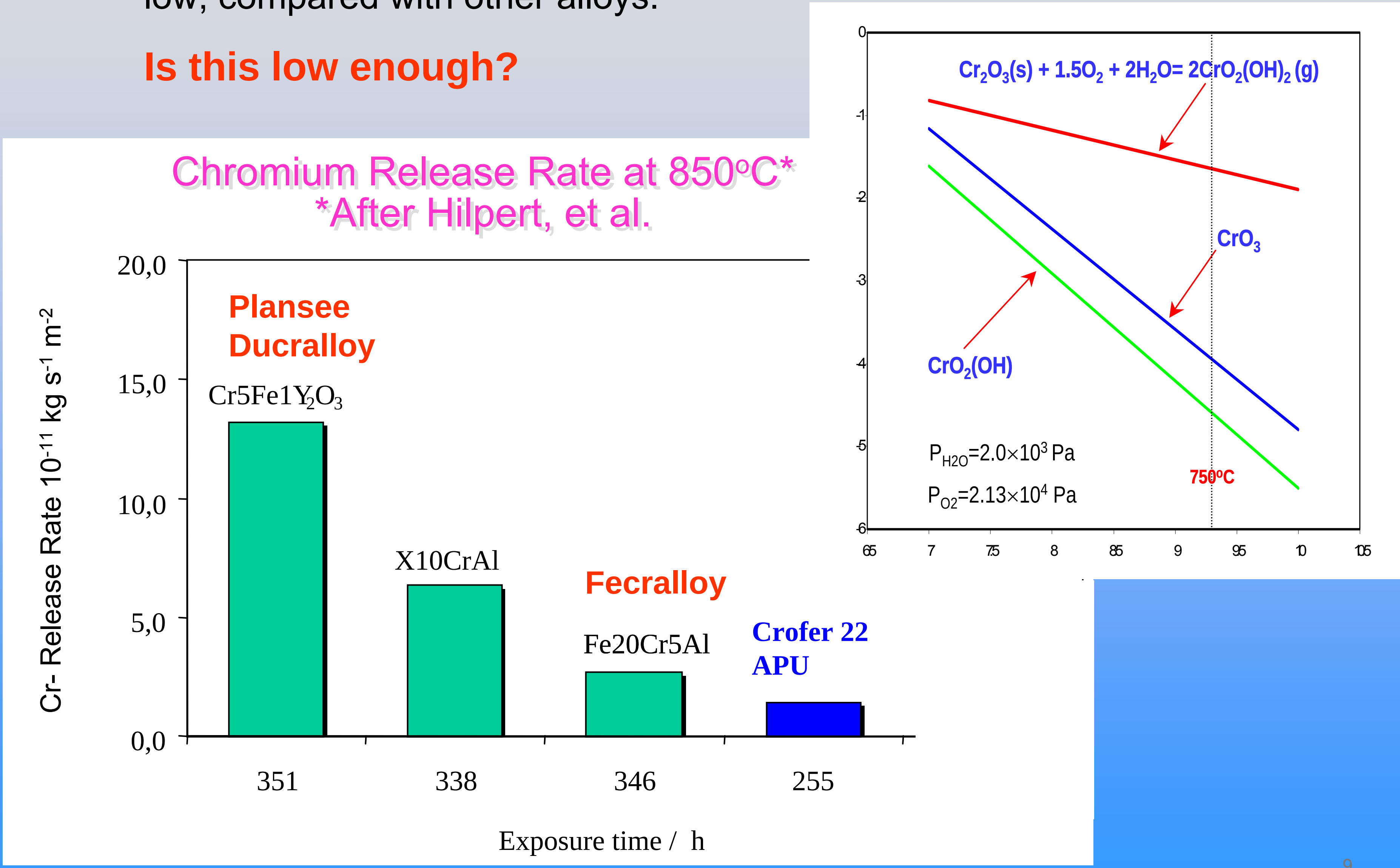




Chromia Scale Evaporation

The chromia evaporation rate is relatively low, compared with other alloys.

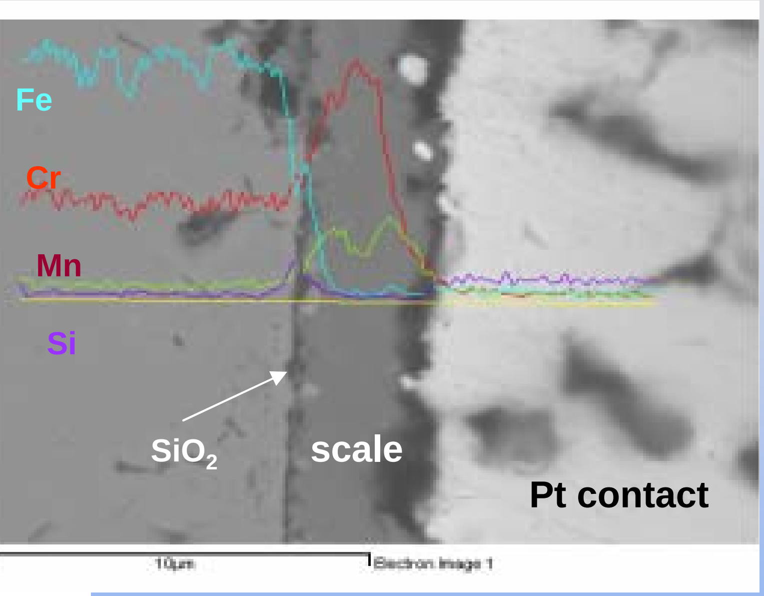
Is this low enough?

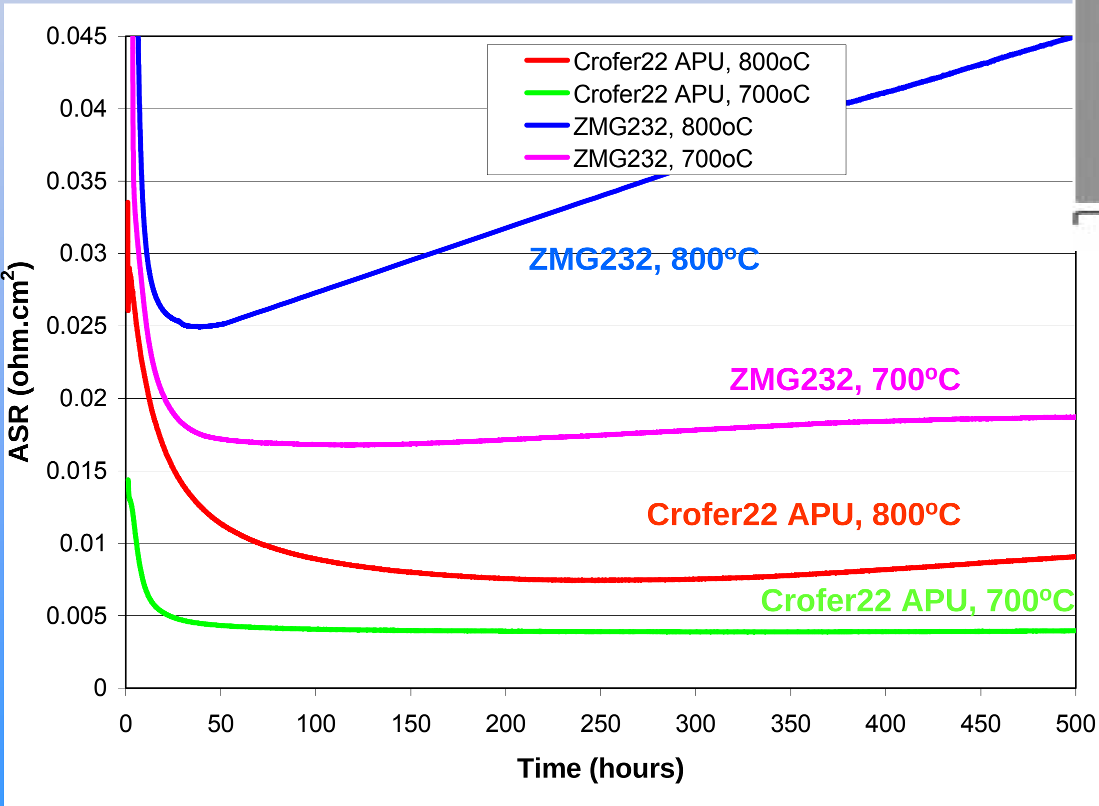


Chromium Release Rate at 850°C*
*After Hilpert, et al.

Evaluation of ZMG232

FSS	Fe	Cr	Mn	Si	Al	RE
ZMG232	Bal.	22	.5	0.40	.21	0.04La 0.22Zr
Crofer22 APU	Bal.	22	.5	--	--	0.06La





The Si level in ZMG232 is enough to form a silica layer that leads to an increased electrical resistance.

Summary

Newly developed ferritic stainless steels demonstrate:

- Good CTE matching;
- Reduced scale electrical resistance;
- Increased scale adherence;
- Decreased chromia evaporation.

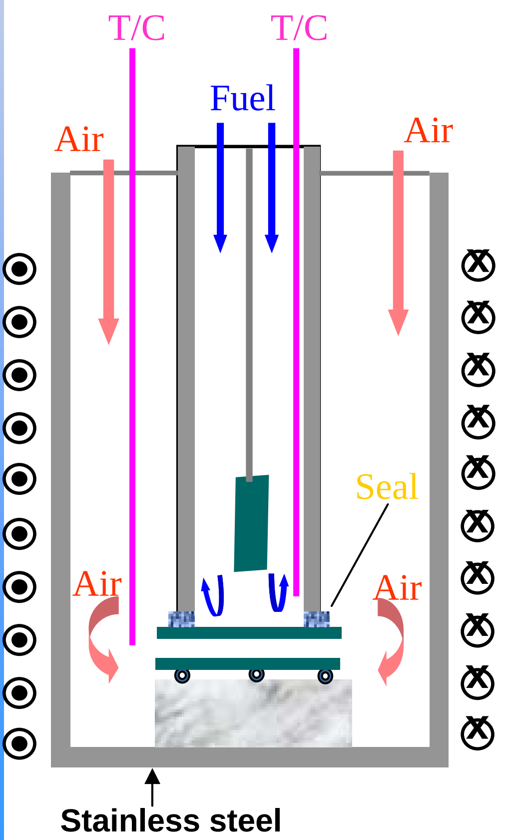
There is HOWEVER, a need for further improvement in:

- Scale electrical conductivity in the long term;
- Scale evaporation;
- Scale adherence and sealing effectiveness;
- Corrosion resistance under dual environments.

For >700°C applications

Dual Atmosphere Study

	FSS	Fe	Ni	Cr	C	Mn	Si	Mo	W	Ti	Al	RE
FeSS	AISI430	Bal.	--	16.0	0.1	1.0	1.0	--	--	--	--	--
	Crofer22 APU	Bal.	--	22.0	0.005	0.5	--	--	--	0.08	--	0.06La
	E-brite	Bal.	--	26.0	0.001	0.01	0.025	--	--	--	--	--
NiBS	Haynes 230	1.5	Bal.	22.0	0.10	0.5	0.4	1.4	14	--	0.3	0.02La .005B



Variables:

Temperature, 700~800^{o}C

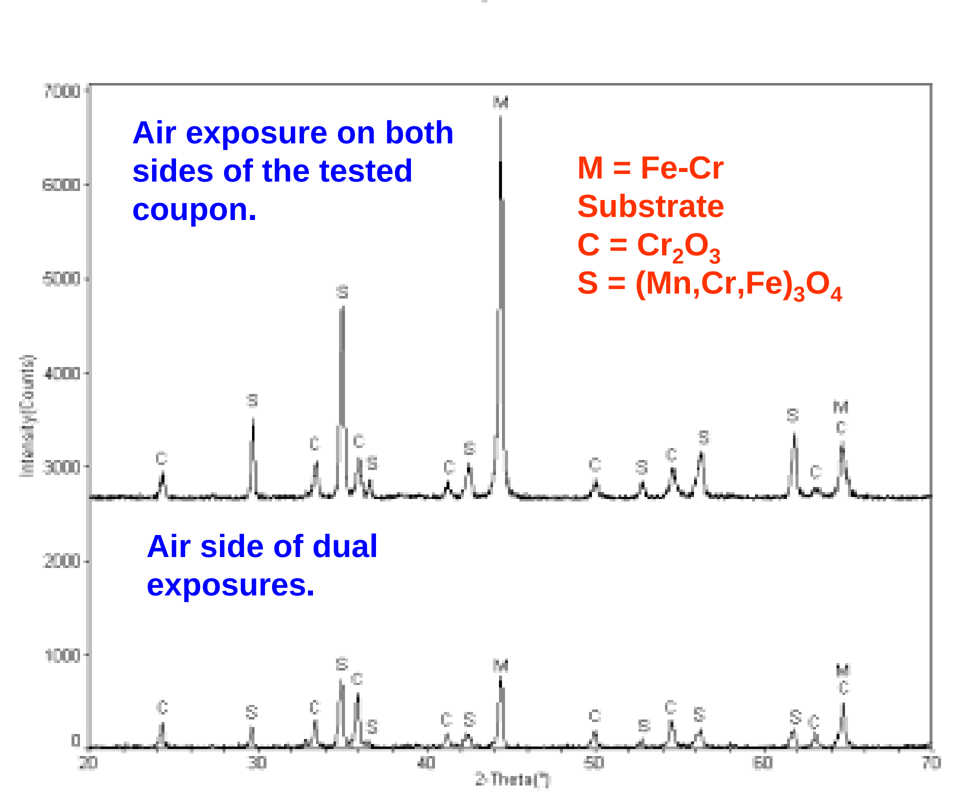
Time, 300 hours

Fuel, H_2+3% H_2O

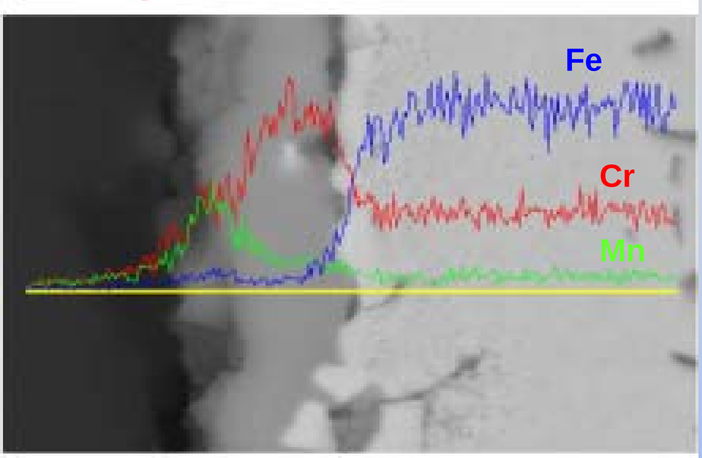
Heating, isothermal and cycling.

Crofer22 APU: Structure of Scales

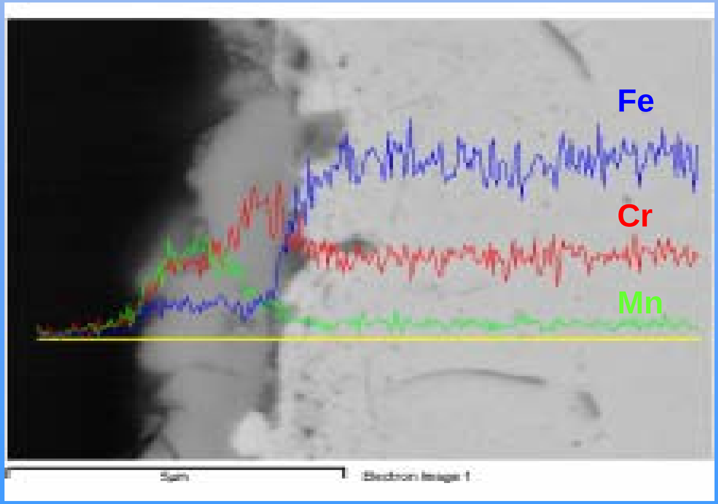
Grown on the coupon in air only and on the air side of the coupon that was ISOTHERMALLY heat-treated at 800ºC, 300 hours.



Air exposure at both sides

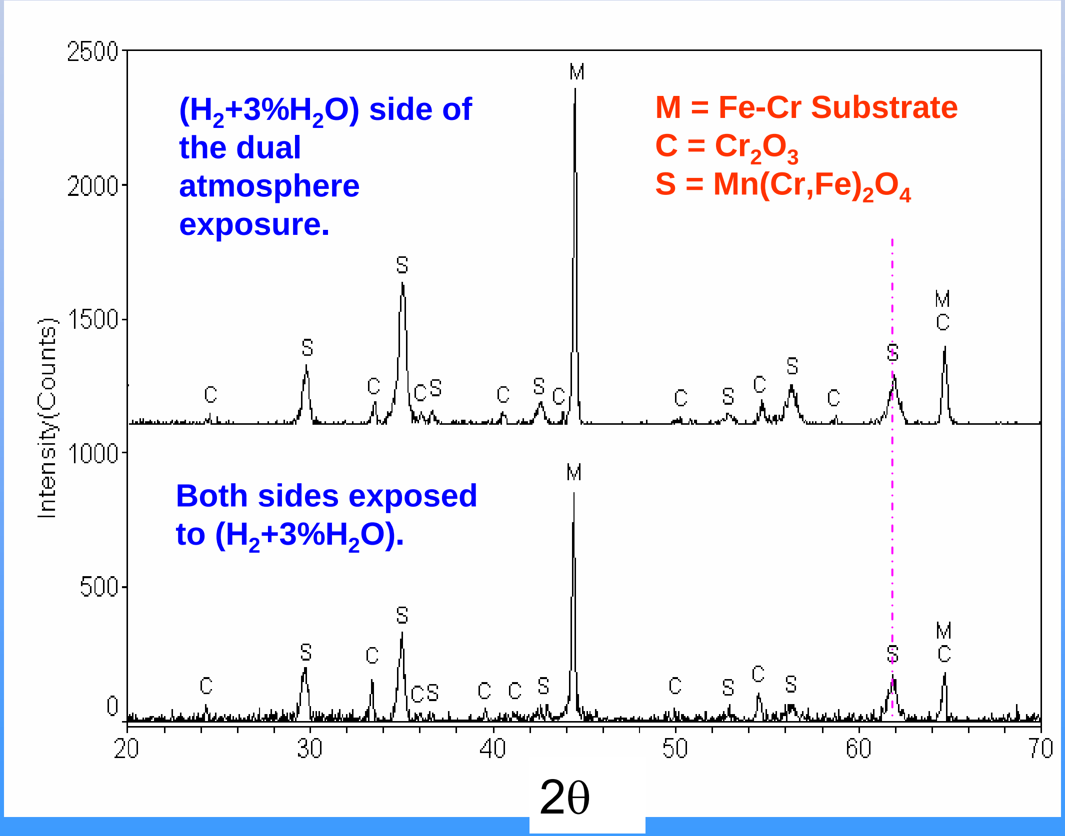


Air-side of dual exposures

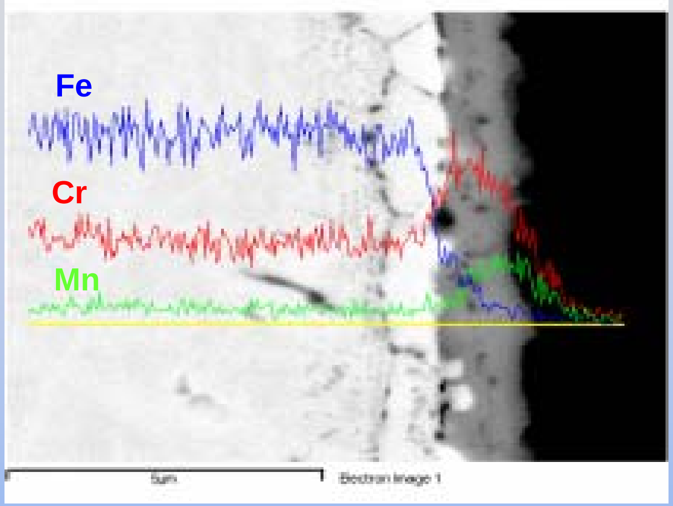


Crofer22 APU: Structure of Scales

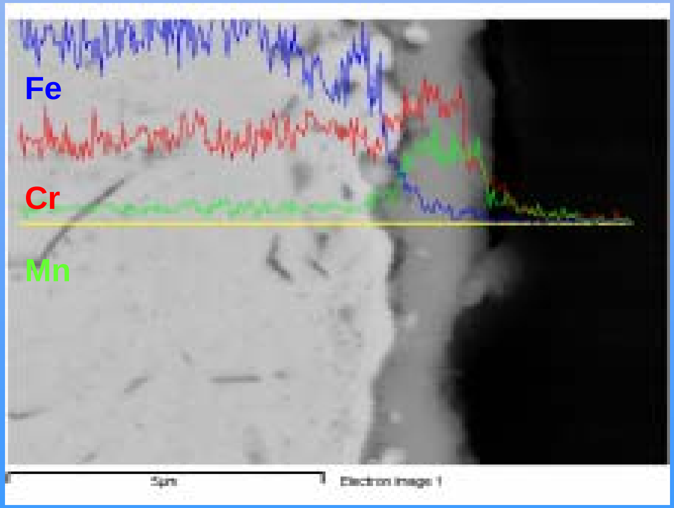
Grown on the coupon in fuel (H_2+3%H_2O) only and on the fuel side of the coupon that was **ISOTHERMALLY** heat-treated at 800ºC, 300 hours.



Fuel exposure at both sides

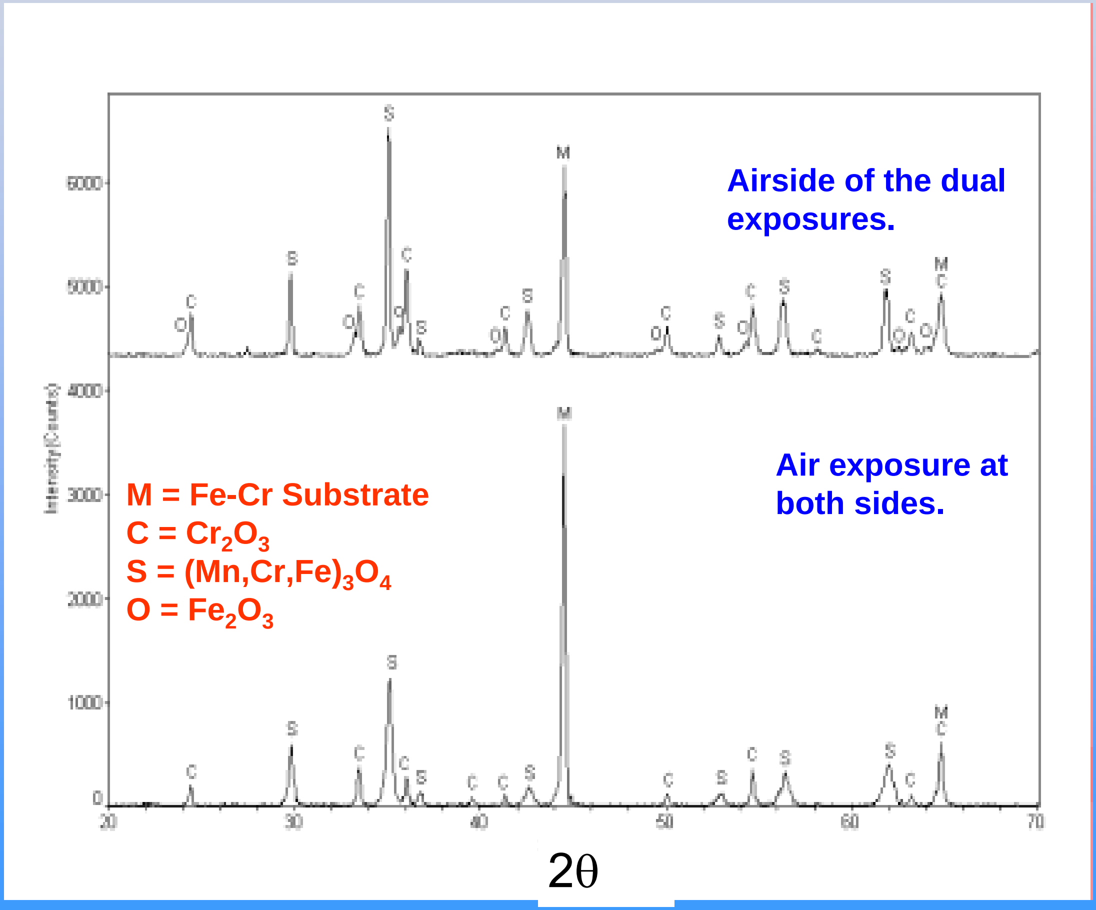


Fuel side of dual exposures

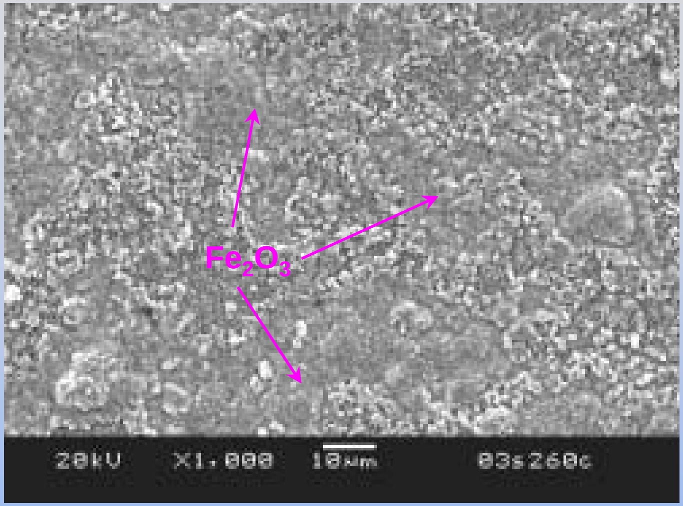


Crofer22 APU: Structure of Scales

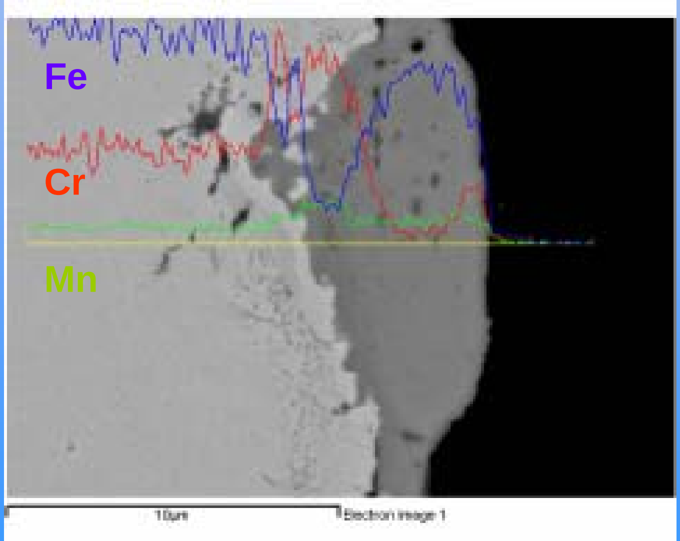
Grown on the coupon in air only and on the air side of the coupon that was heat-treated at 800ºC for 300 hours, with three thermal cycles.



Air-side of dual test



Cross-section: airside of dual test

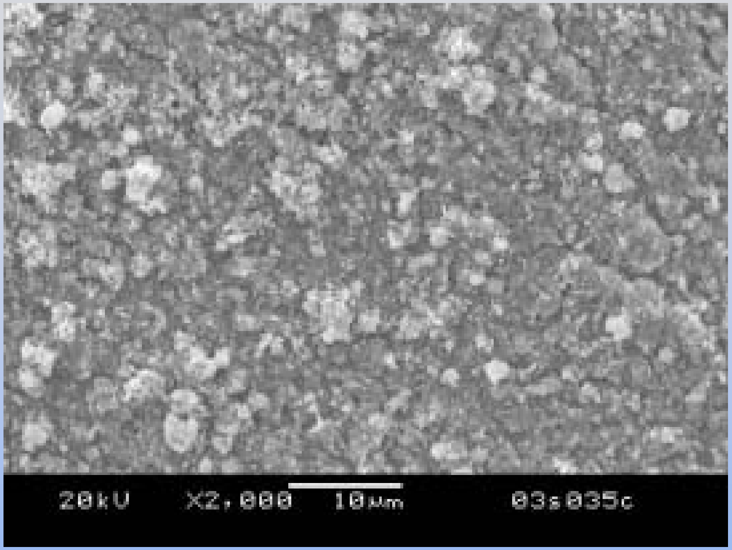


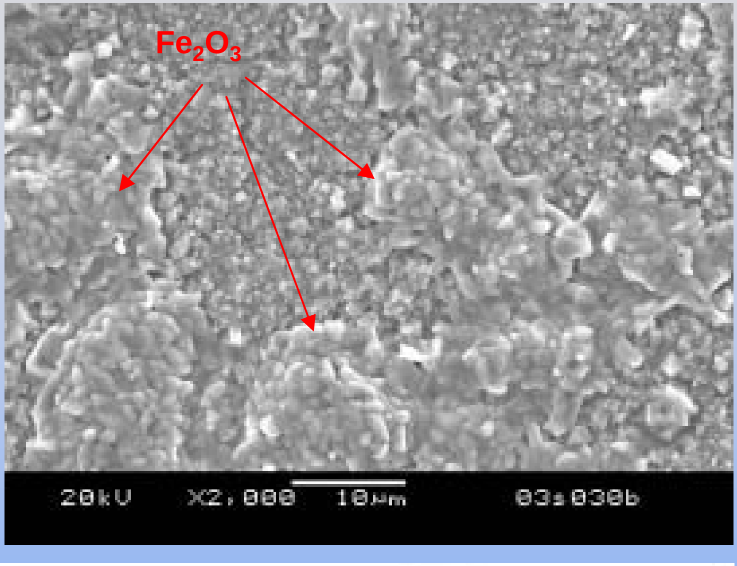
AISI430: Scale Microstructures

Air exposure at both sides

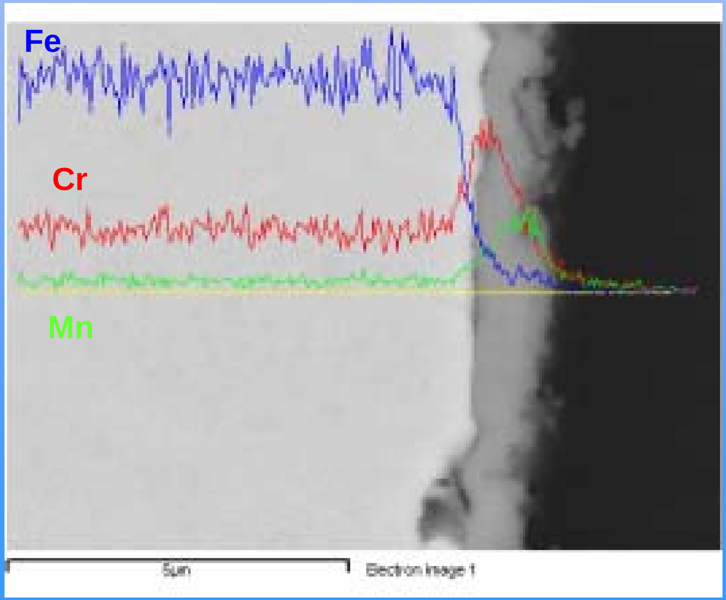
Air-side of dual exposures

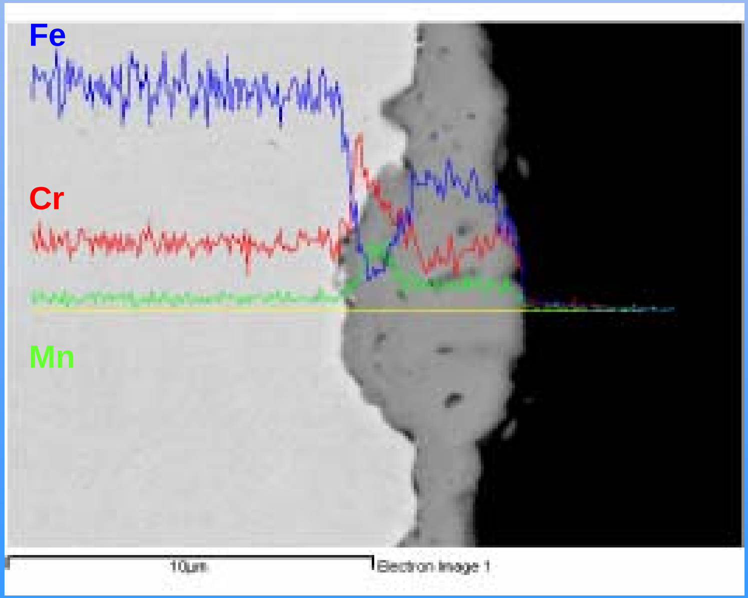
Surface microstructures





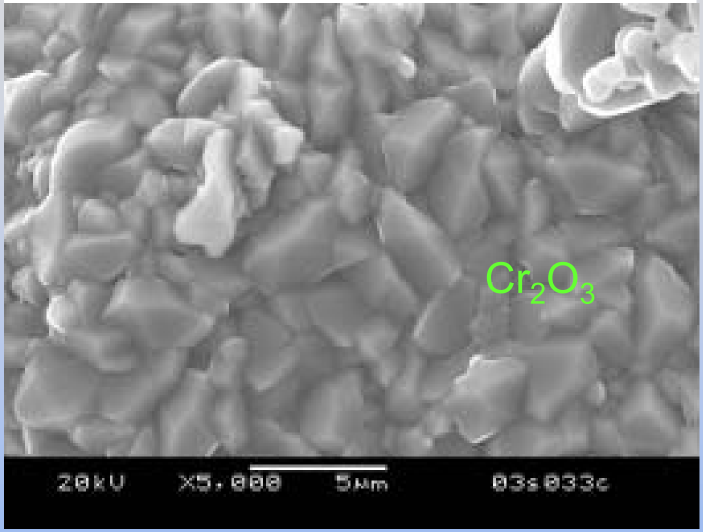
Cross-sections



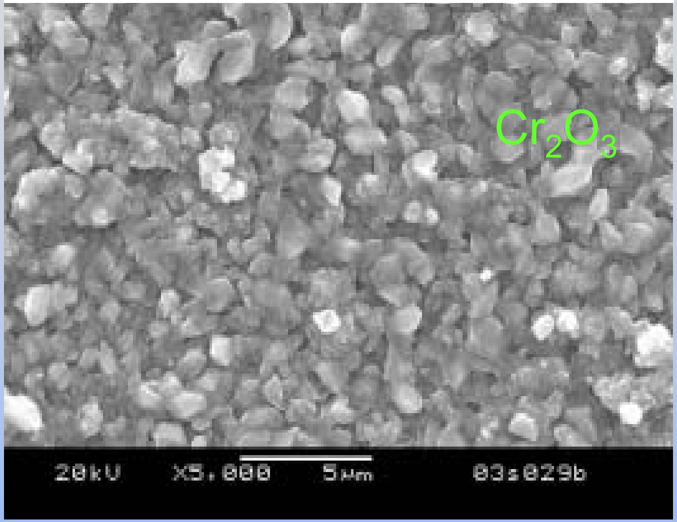


E-brite: Scale Microstructures

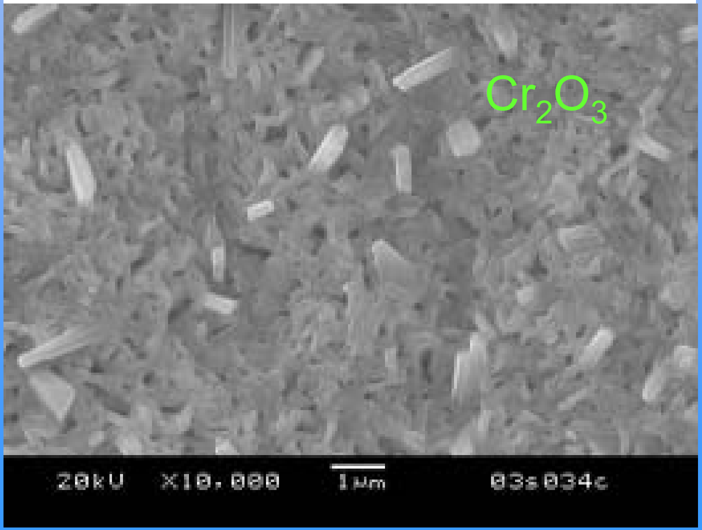
Air exposure at both sides



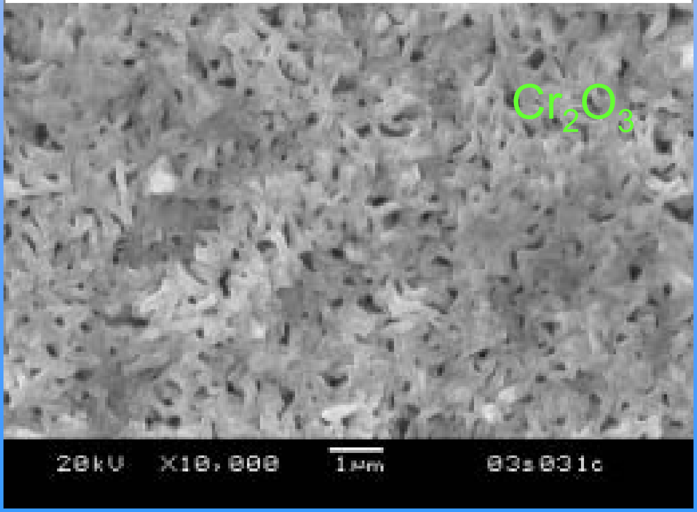
Air side of dual exposures



(H_2+3%H_2O) at both sides

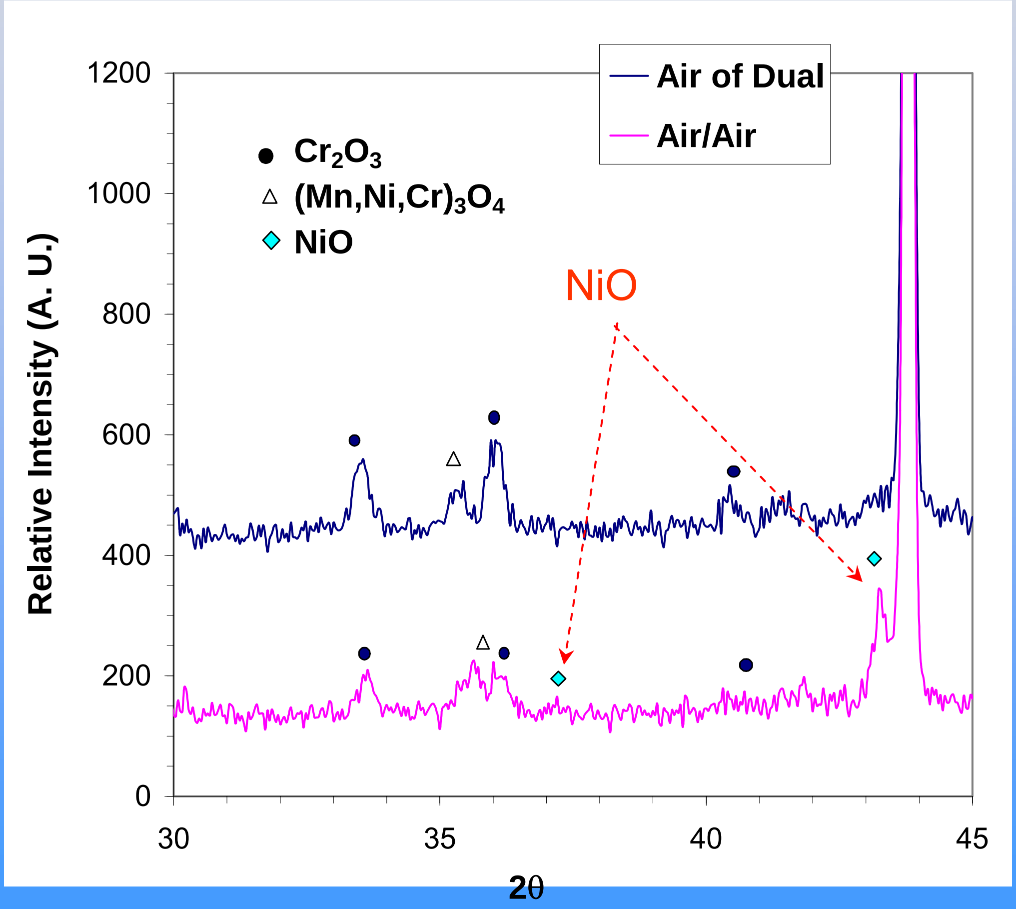


Fuel side of dual exposures

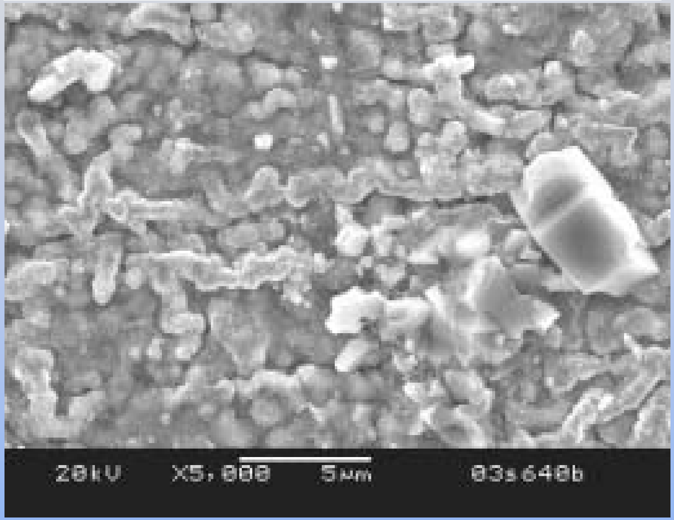


Haynes230: Structure of Scales

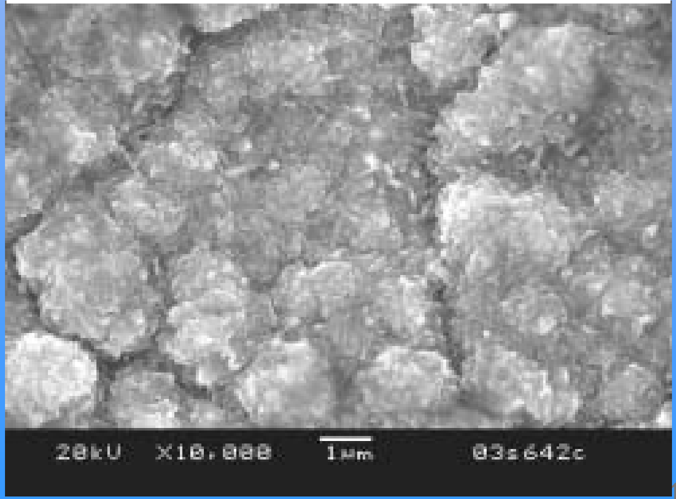
Grown on the coupon in air only and on the air side of the coupon that was isothermally heat-treated at 800°C, 300 hours.



Air exposure at both sides



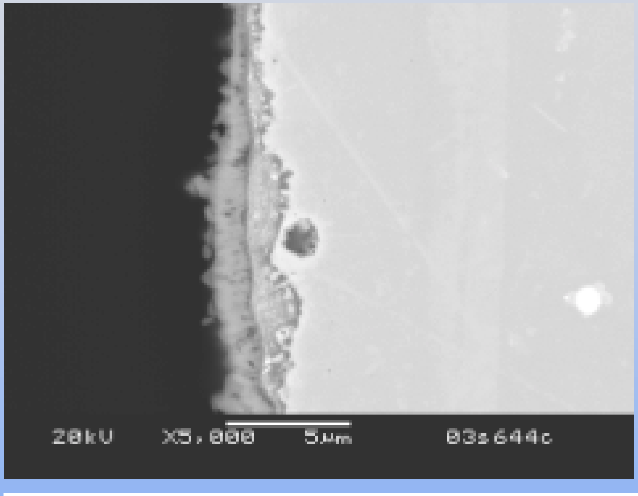
Air side of dual exposures

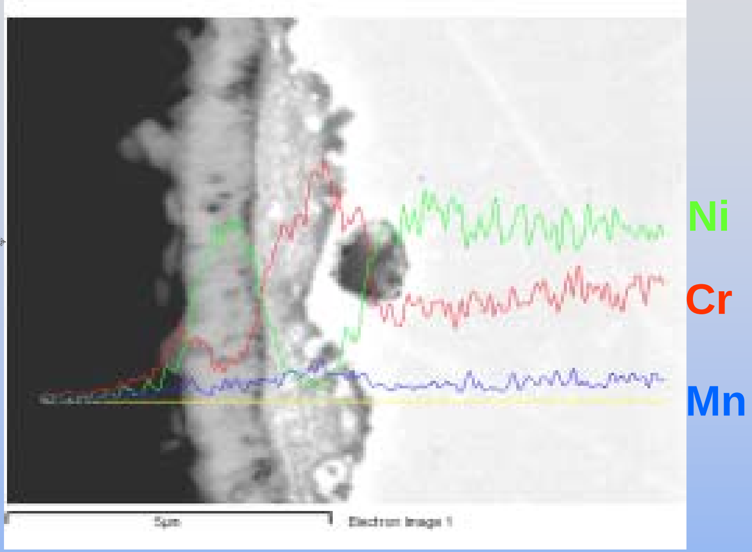


Haynes230: Cross-Sections

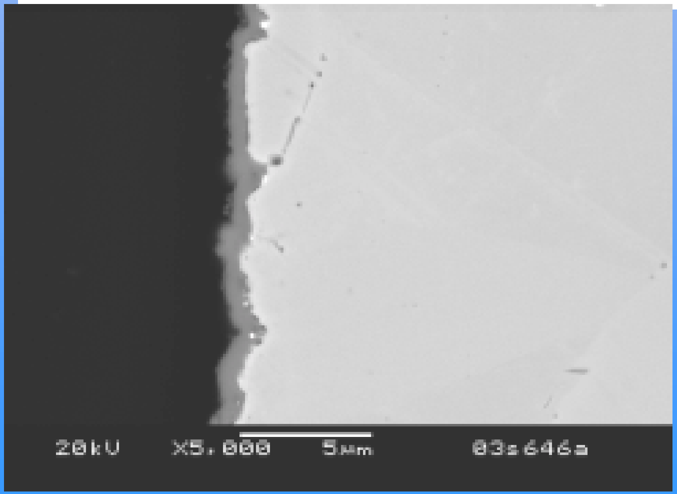
Grown on the coupon in air only and on the air side of the coupon that was isothermally heat-treated at 800°C, 300 hours.

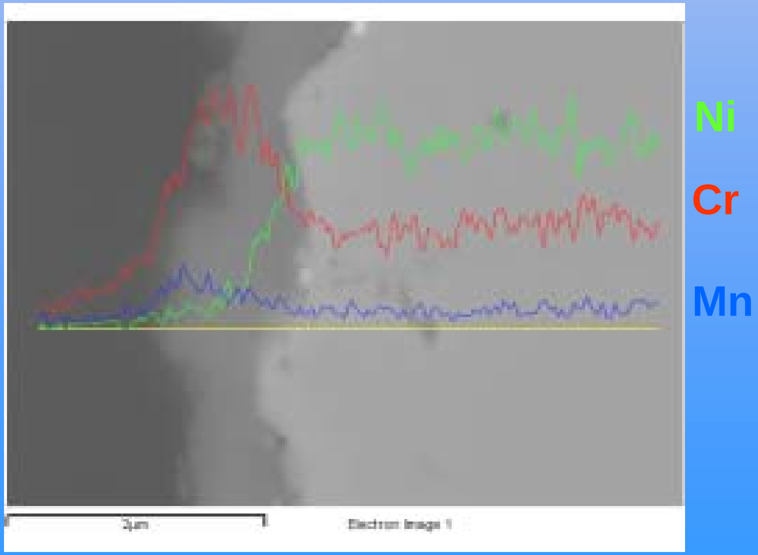
Air exposure at both sides





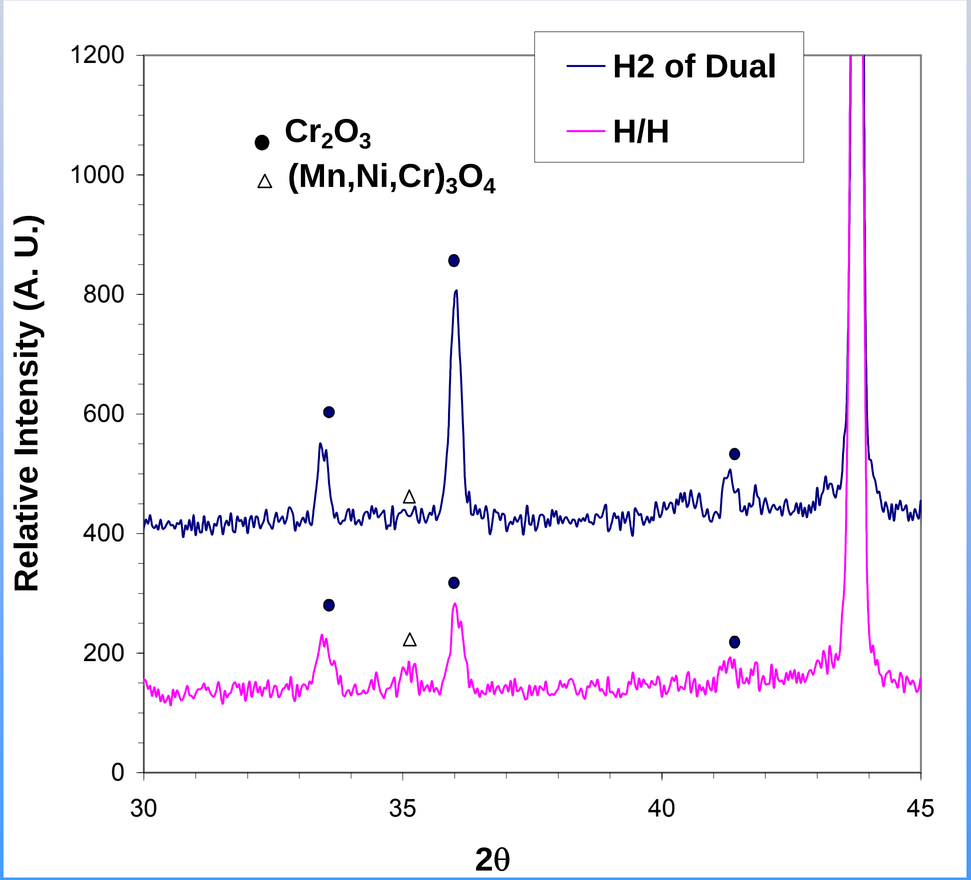
Air side of dual exposures



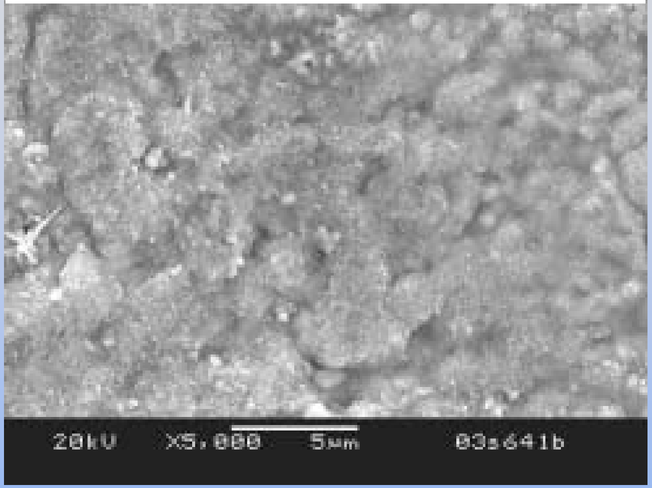


Haynes230: Structure of Scales

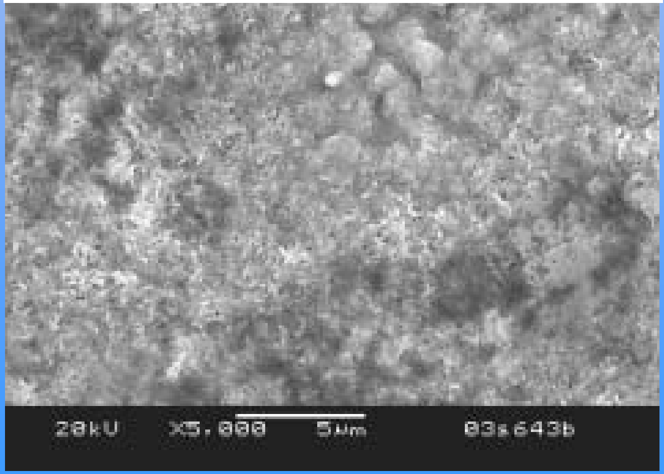
Grown on the coupon in fuel only and on the fuel side of the coupon that was isothermally heat-treated at 800°C, 300 hours.



$(H_2+3\%H_2O)$ at both sides



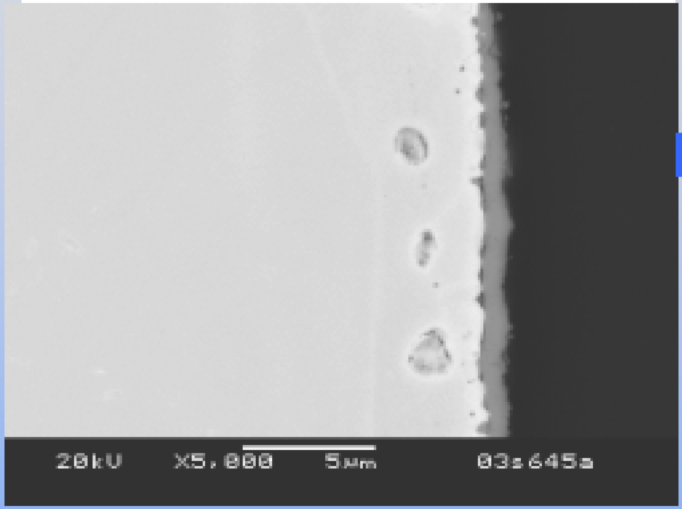
Fuel side of dual atmospheres

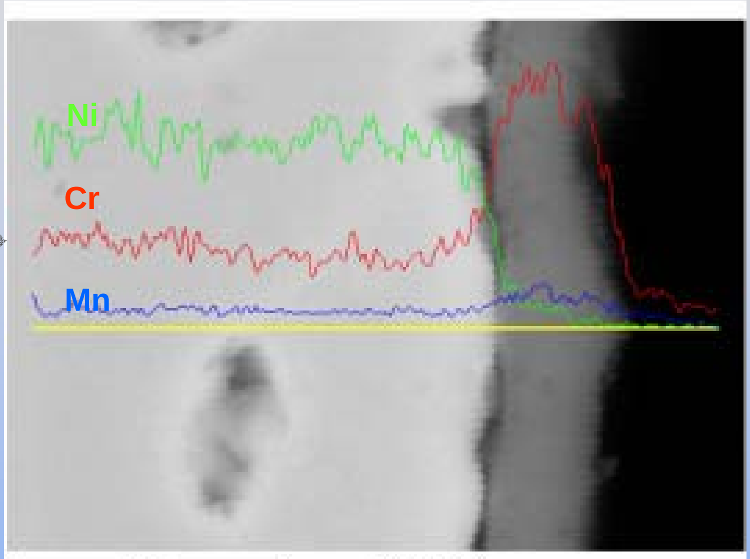


Haynes230: Cross-Sections

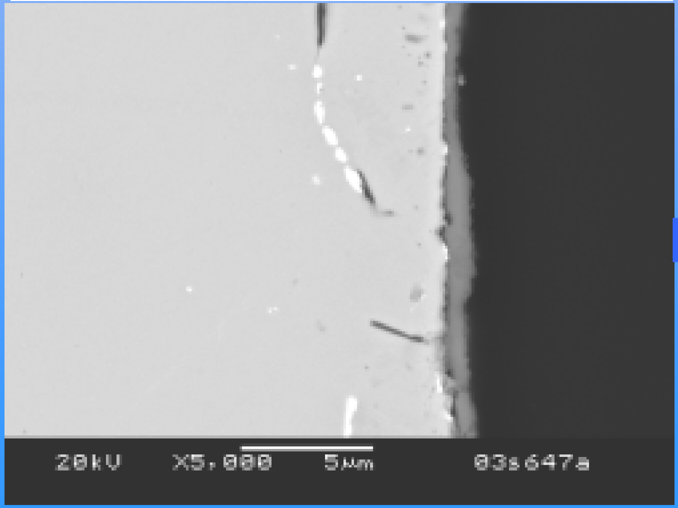
Grown on the coupon in fuel only and on the fuel side of the coupon that was isothermally heat-treated at 800°C, 300 hours.

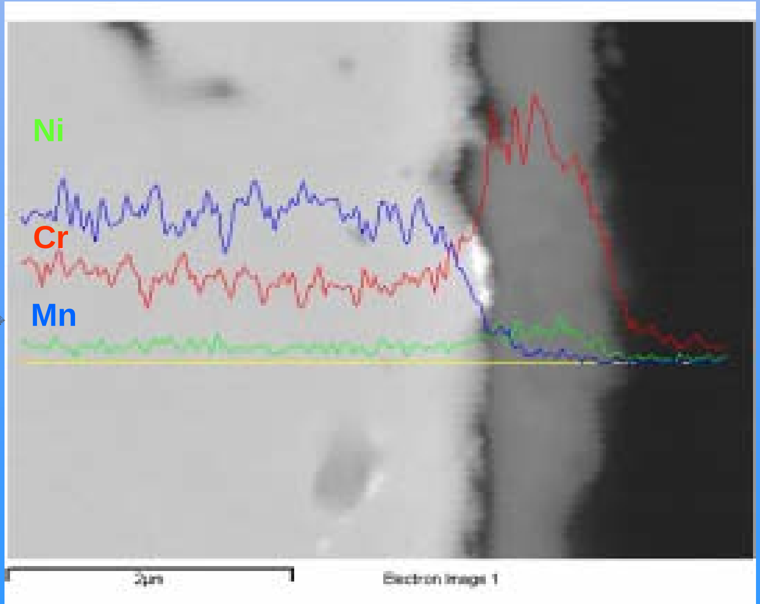
Fuel exposure at both sides





Fuel side of dual atmospheres



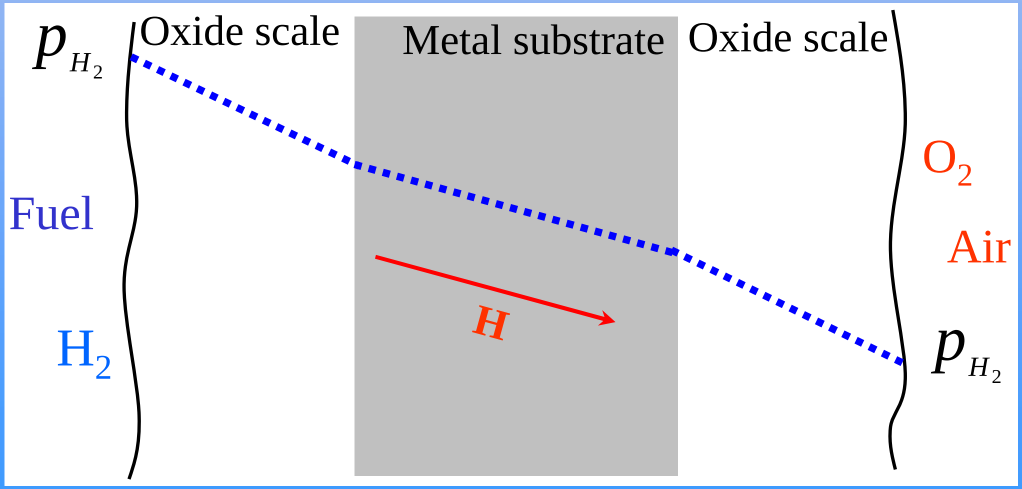


Summaries

The Dual Atmosphere exposure can lead to an anomalous oxidation/ corrosion behavior of oxidation resistant alloys:

For **ferritic stainless steels** with relative low chromium level, dual exposure enhances the iron transport in scale on the airside, leading to hematite formation and a locallized attack.

For **Ni-based superalloys**, e.g. Haynes230 with 22% Cr, dual exposure facilitates the formation of a uniform chromia dominated scale.



Comparison

	Haynes230 **Ni-base superalloy** **Ni-22Cr-14W-2Mo-.5Mn**	**Crofer22 APU** **Stainless steel** **Fe-22Cr-.5Mn**
Thermal expansion X10^{-6}.K^{-1}	**15.2** RT-800°C	**12.2** RT-800°C
Oxidation resistance Kg, 10^{-13} .g^{2} .cm^{-4} .s^{-1}	**0.36**, 800°C **0.05**, 700°C	**7.0**, 800°C **2.0**, 700°C
ASR, mΩ.cm^{2} After 600h of oxidation	**10.0**, 800°C **5.0**, 700°C	**9.0**, 800°C **4.0**, 700°C
Dual atmosphere Corrosion resistance	Enhanced formation of uniform chromia scale	Grow hematite to accelerate attack
Ultimate tensile stength, σ_u (MPa)	**865**, RT **605**, 760°C	**443**, RT **<100**, 760°C
Manufacturability	Very easy	Fairly easy
Raw materials cost	Fairly expensive	Inexpensive

Future Work

Identifying Issues and Understanding

- Continue the systematic screening studies, with emphasis on dual atmosphere studies, including extension of dual atmosphere studies to air vs. reformate inveironments.
- Study scale evaporation.

Materials Development

- Modifications (bulk and/or surface) to Fe and Ni based alloys
- Cathode/interconnect interfaces.

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