Effect of H_2O and CO_2 on the Selective Oxidation of Iron Base and Nickel Base Alloys

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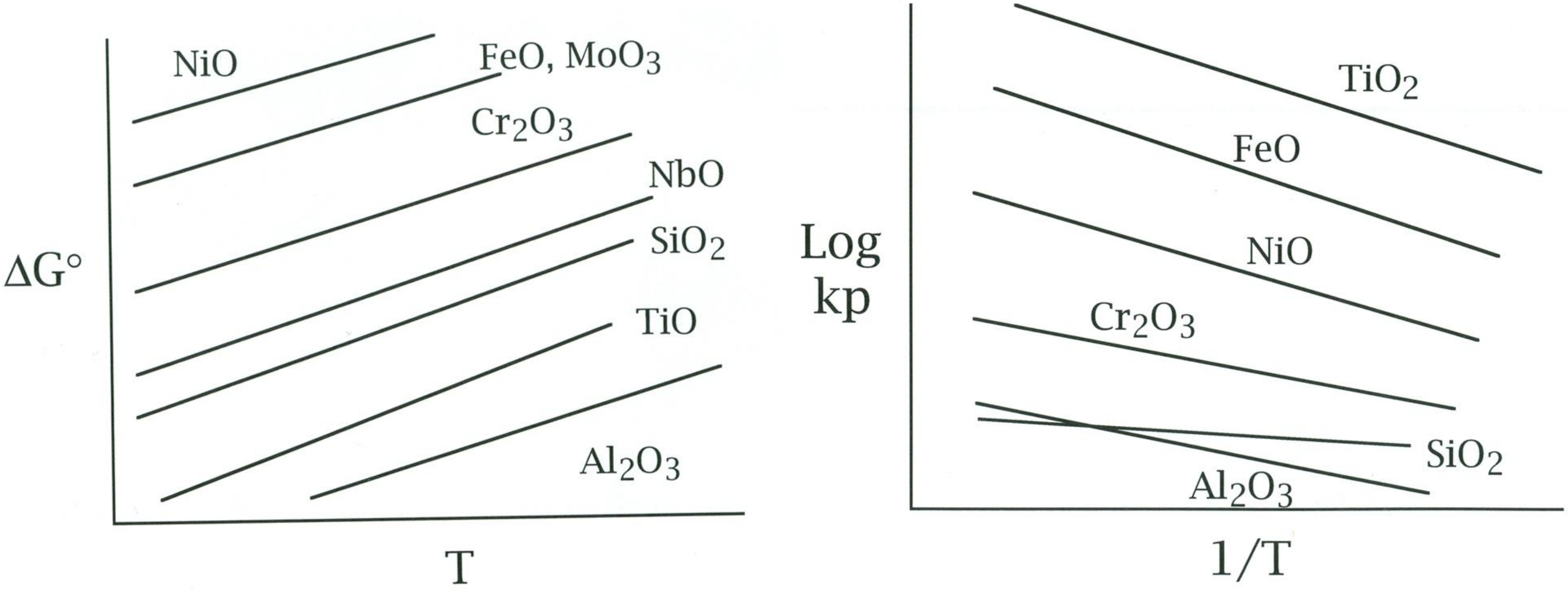
Statement of the Problem

1. The use of oxygen, instead of air, in oxy-fuel systems, will significantly change the compositions of the gas in the combustion chamber.

2. The gas phase will be rich in H_2O(g) and CO_2(g) which can have dramatic effects on alloy corrosion behavior.

Thermodynamic and Kinetic Data

Increasing Stability

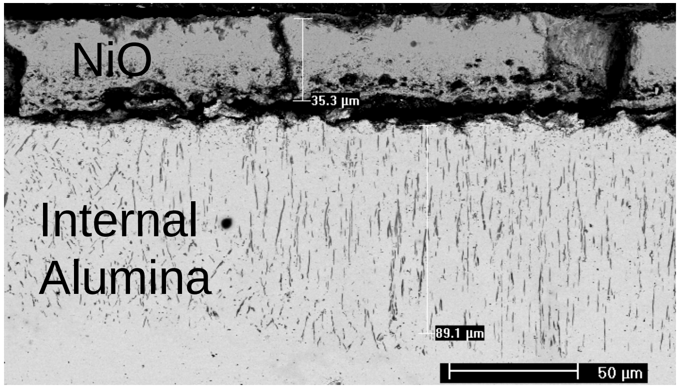


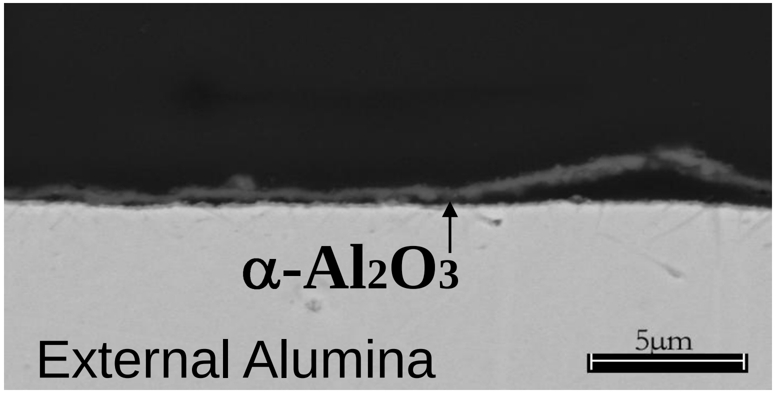
Decreasing growth Rate

Selective Oxidation

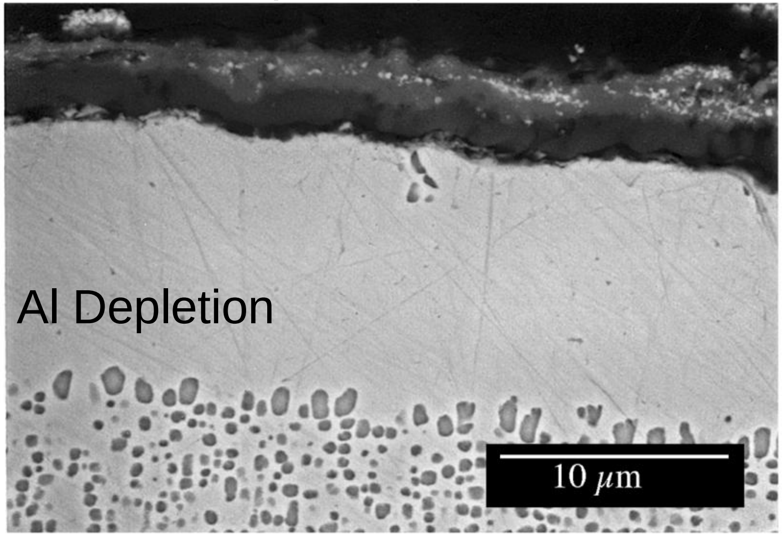
$$N_{Al}^{(o)} > \left[\frac{\pi g^*}{2\nu} N_O^{(S)} \frac{D_O V_m}{D_{Al} V_{ox}}\right]^{1/2}$$

Ni-Al





Superalloy



← Transient Oxide

← Alumina

$N_{Al}^{(o)} \uparrow$ as $k_P^{Trans} \uparrow$

$$N_{Al}^{(o)} = \frac{V_m}{32\nu}\left(\frac{\pi k_p}{D_{Al}}\right)^{1/2}$$

To Maintain Continuous Alumina

Selective oxidation of Cr from Fe-Cr and Ni-Cr alloys

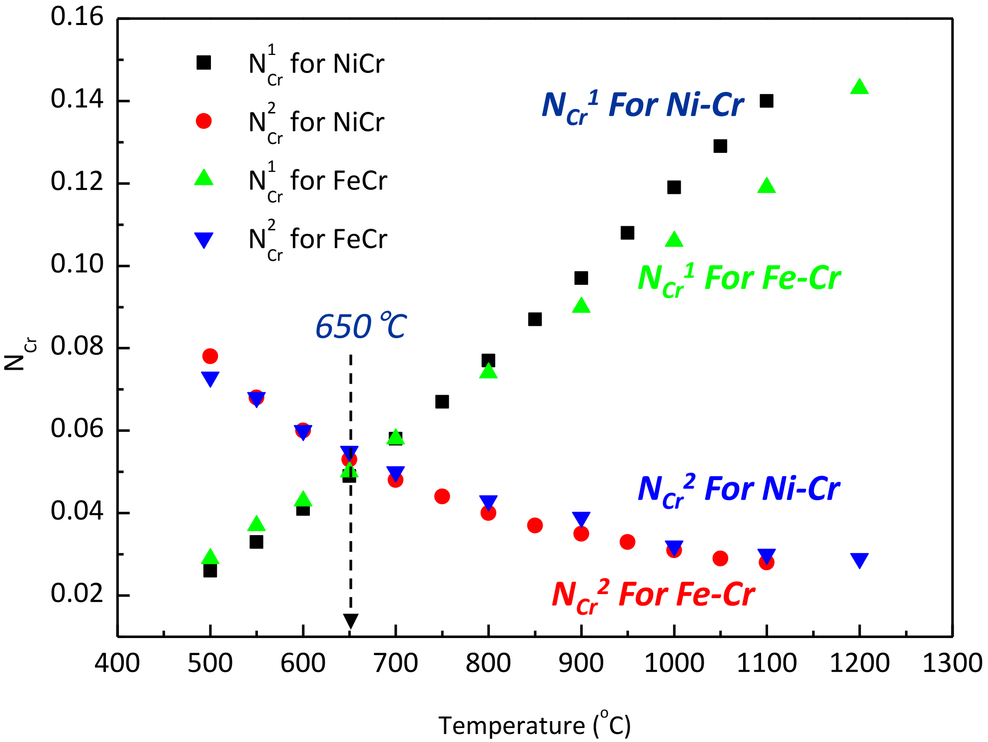
Two criteria to form and maintain a continuous Cr_2O_3 scale on an M-Cr alloy (M = Fe, Ni or Co)

Suppression of internal oxidation of Cr:

$$N_{Cr}^{(1)} > \left[\frac{\pi g^{*}}{3} N_O^{(S)} \frac{D_O V_m}{\tilde{D}_{M-Cr} V_{CrO_{1.5}}}\right]^{1/2} \qquad \text{.... (1)}$$

Supply sufficient Cr to surface:

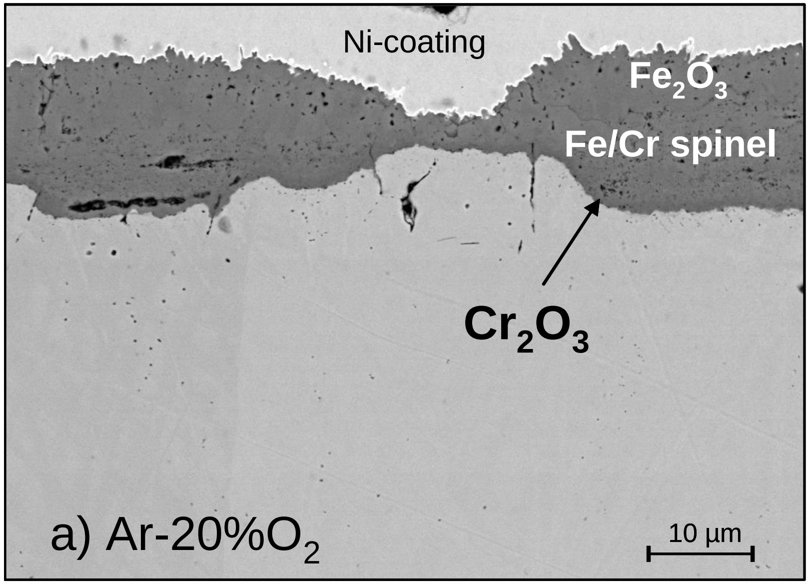
$$N_{Cr}^{(2)} = \frac{V_m}{32\nu}\left(\frac{\pi k_p}{\tilde{D}_{M-Cr}}\right)^{1/2} \qquad \text{.... (2)}$$

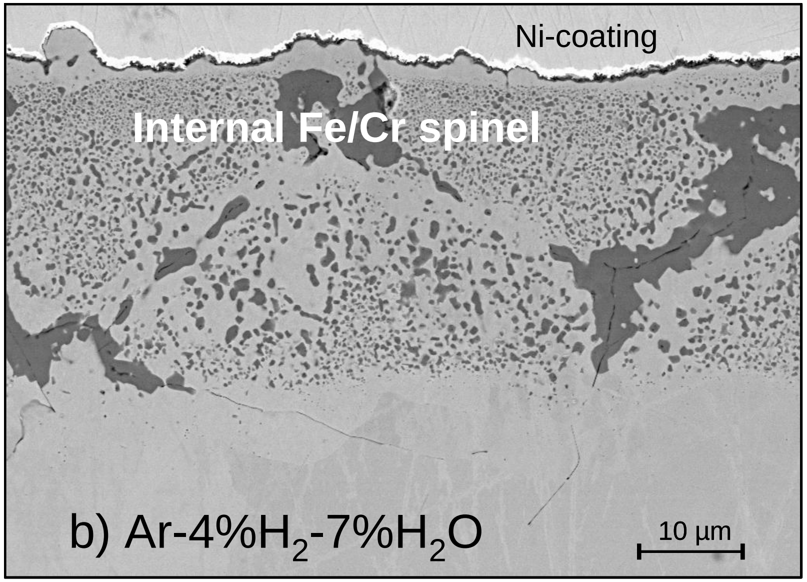


Based on the calculations, about 6-8% Cr are required for external Cr_2O_3 formation on both Fe-Cr and Ni-Cr alloys in the temperature range 500-700°C.

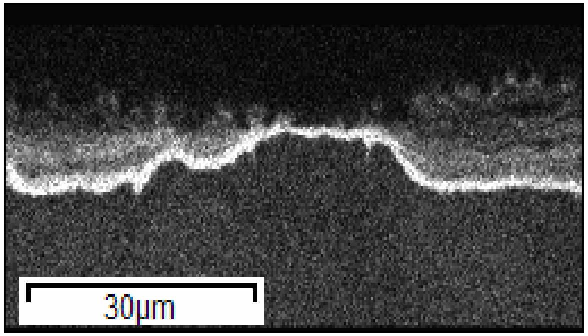
Effect of Water Vapor on Selective Oxidation

Oxidation of Fe-10Cr at 900°C





$p_{O2} \approx 10^{-15}$ atm



Cr Map

E. Essuman, G.H. Meier), J. Żurek, M. Hänsel, L. Singheiser, W.J. Quadakkers “Enhanced internal oxidation as trigger for breakaway oxidation of FeCr-alloys in water vapor containing gases”, Scripta Mat., 57, 845 (2007).

Proposed Effects of H_2O on Selective Oxidation of Cr

- **Effects Based on** $N_{Cr}^{(1)}$

E. Essuman, G.H. Meier), J. Żurek, M. Hänsel, L. Singheiser, W.J. Quadakkers Scripta Mat., 57, 845 (2007).

Proposed effects on oxygen permeability

M. H. B. Ani, T. Kodama, M. Ueda, K. Kawamura, and T. Maruyama, *Mater. Trans. (Japan)*, 50, 256 (2009).

Measured $\tilde{D}_{Fe-Cr}$ **Unaffected by H_2O**

Found $N_O^{(S)} D_O$ **increased by a factor of 1.4 in H_2O in Fe-5Cr**

Internal oxide particles were elongated in H_2O

Hydrogen Injection During Oxidation by Water Vapor

- **A. Rahmel and J. Tobolski, *Corrosion Sci.*, 5, 333 (1965).**

  Dissolved hydrogen content in Fe increased during H_2O oxidation

- **C. T. Fujii and R. A. Meussner, *J. Electrochem. Soc*., 111, 1215 (1964).**

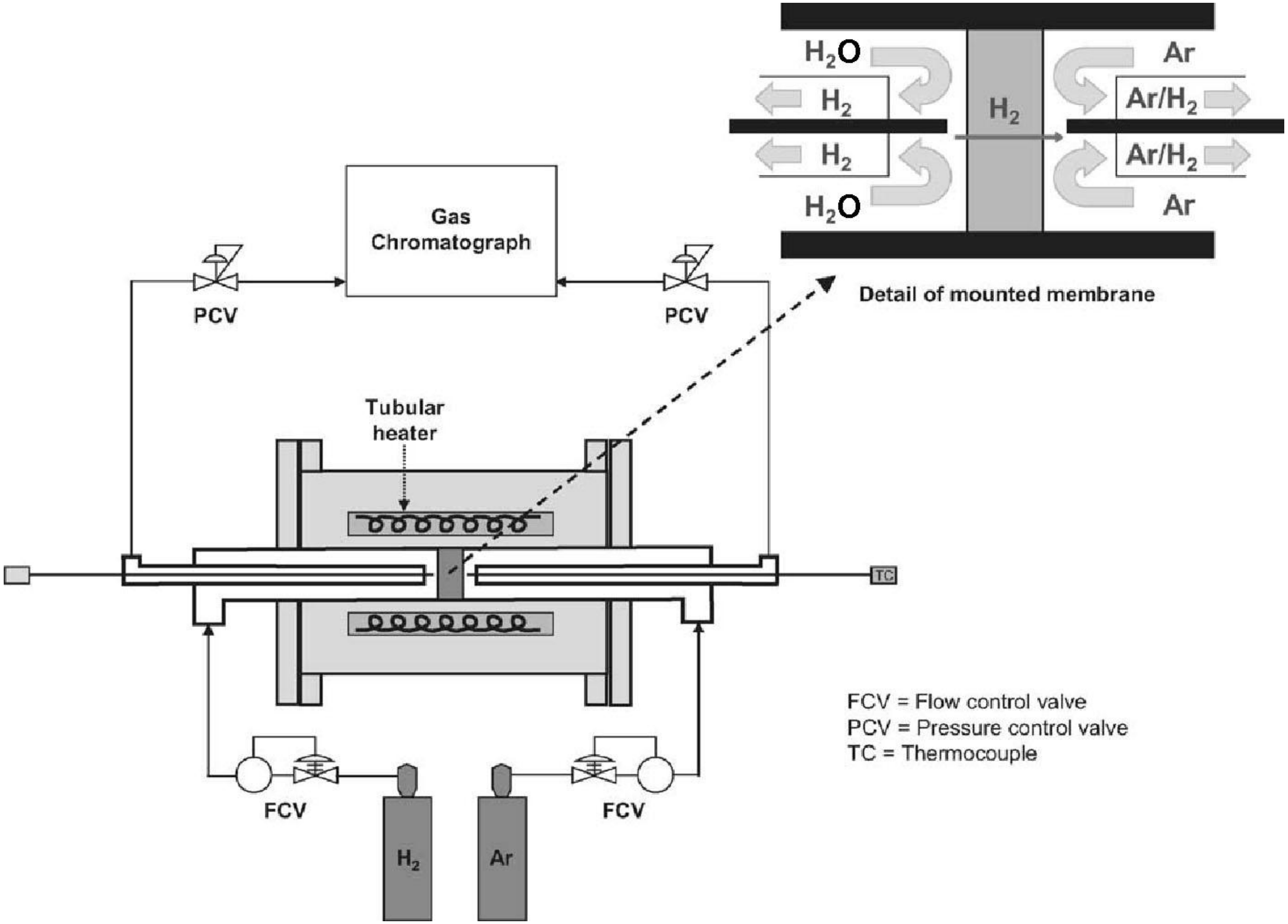
  Detected H_2 inside Fe-5Cr thimble when outside oxidized in H_2O

- **L. Tomlinson and N. J. Cory, *Corrosion Sci.*, 29, 939 (1989).**

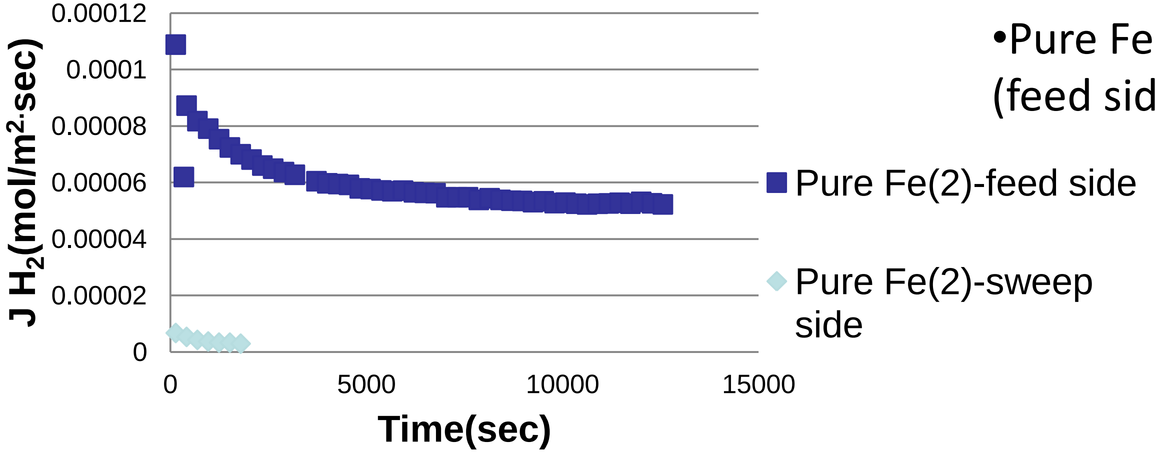
  Oxidized Fe-Cr steel tubes with H_2O inside and a sweep gas outside – measured H_2 both in oxidizing gas and sweep gas

Hydrogen Permeation Testing at NETL

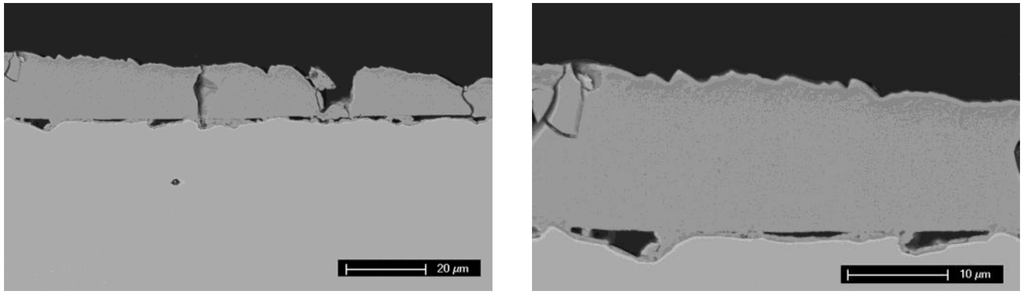
- An existing apparatus at NETL was modified in order to be able to measure the separate rates of hydrogen emission into the gas and into the specimen during oxidation in Ar-H_2O atmosphere by use of Gas Chromatography (GC).



•Several experiments have been performed with Pure Fe and Fe-10Cr specimens.



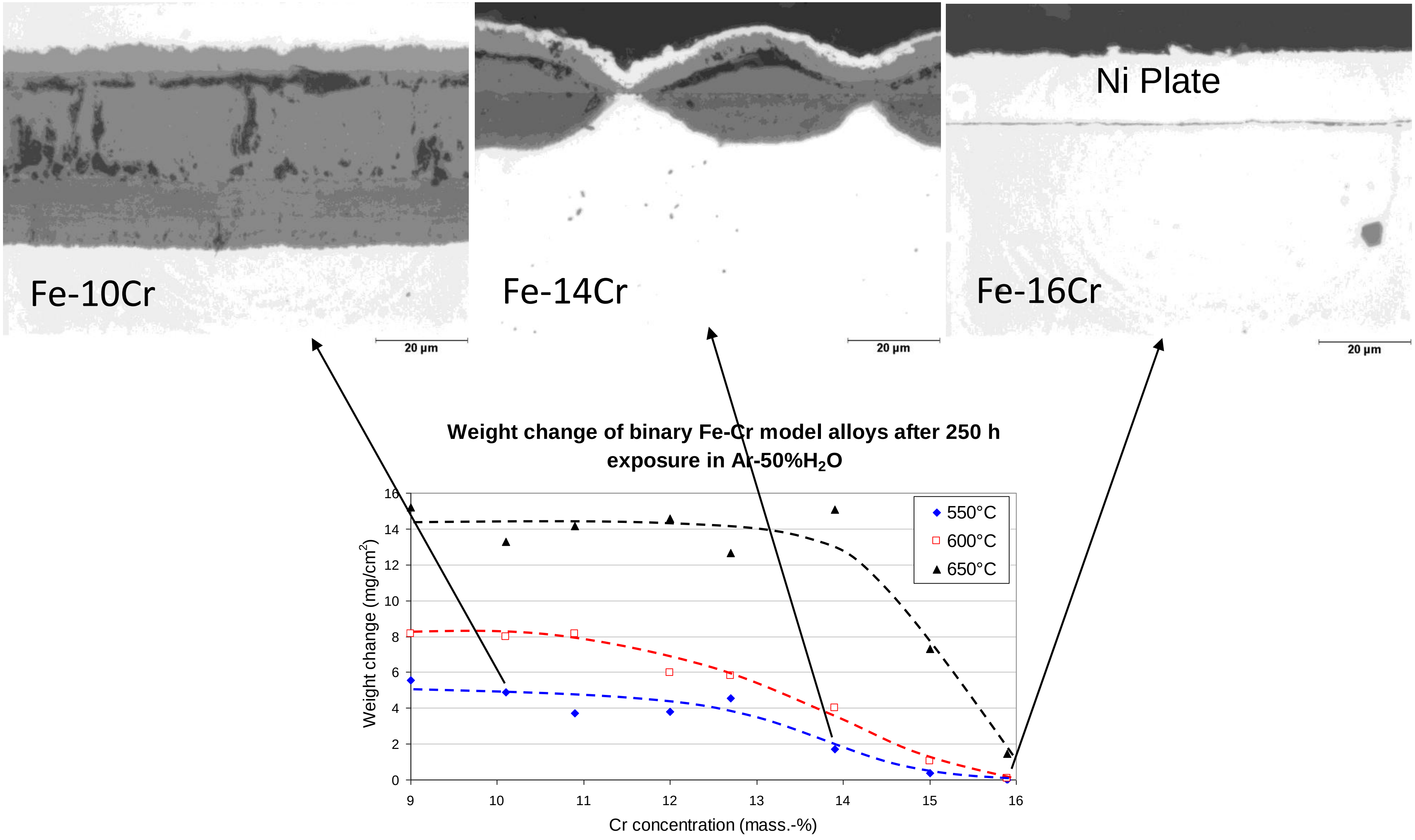
- Pure Fe exposed for 4 hrs @750°C (feed side:Ar-3%H_2O, sweep side:Ar)



- Calculated oxide thickness by using the amount of hydrogen produced is ~10 microns, which is close to the measured thickness.

Fe-Cr Binary model alloys in Ar – 50% H_2O

: Effects of Cr concentration and temperature



Weight change of binary Fe-Cr model alloys after 250 h exposure in Ar-50%H_2O

Proposed Effects of H_2O on Selective Oxidation of Cr

- **Effects Based on** $N_{Cr}^{(2)}$

  Enhanced Evaporation as $CrO_2(OH)_2$

  (Cannot be relevant for O_2-free atmospheres)

- Accelerated Chromia Growth

  N. K. Othman, J. Zhang and D. J. Young, *Oxid. Metals*, 73, 337 (2010).

  (Presumes initial development of continuous chromia)

Experimental Details

A. Alloy compositions (wt.%)

- Model Alloys (Grain size: 30-100 μm)

  Fe-(8-22)%Cr, Fe-22%Cr-(1-4)%Ti (ferritic)

  Fe-12%Ni-18%Cr (austenitic); Ni-22%Cr

- Commercial Alloys

alloys	Fe	Cr	Ni	Mo	C	Mn	V	Si	other
T91	89.2	8.64	0.13	0.94	0.103	0.43	0.20	0.32	0.14Cu
T92	87.8	8.90	0.23	0.38	0.123	0.43	0.20	0.28	1.83W
P92	88.1	8.90	0.23	0.38	0.07	0.43	0.20	0.30	1.20W
IN617	2.24	21.6	54.6	7.74	0.102	0.036	-	-	10.9Co

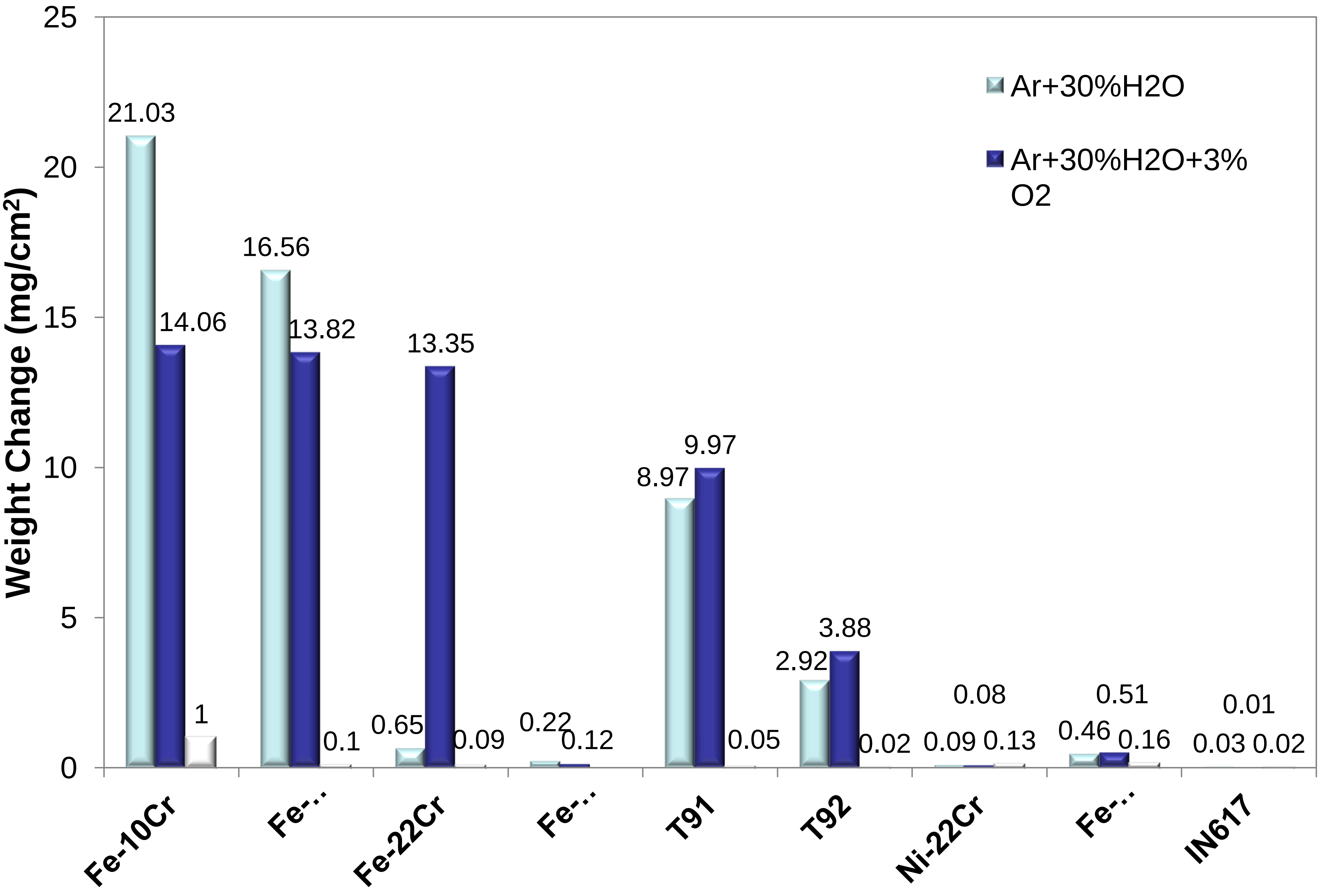
B. Gas compositions (vol.%)

	Gas compositions
1	Dry air
2	Ar-30%CO_2
3	Ar-30%H_2O
4	CO_2-30%H_2O
5	Ar-CO_2+ Excess O_2
6	CO_2-H_2O + Excess O_2

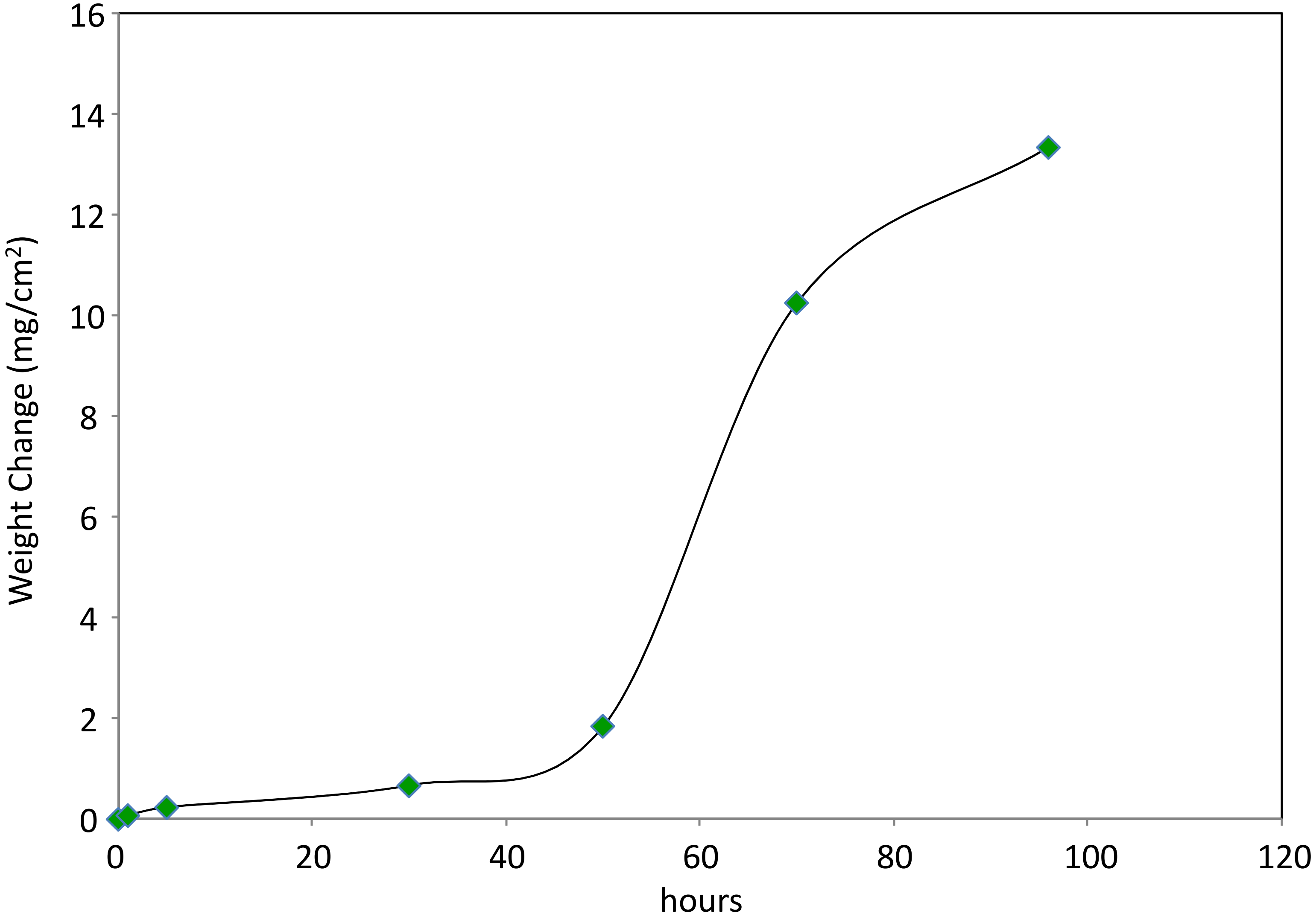
C. Exposure test

- pseudo-isothermal exposure at 650°C.
- mass changes measured after every 4 day exposure.

Gas Velocity ≈ 1 cm/sec

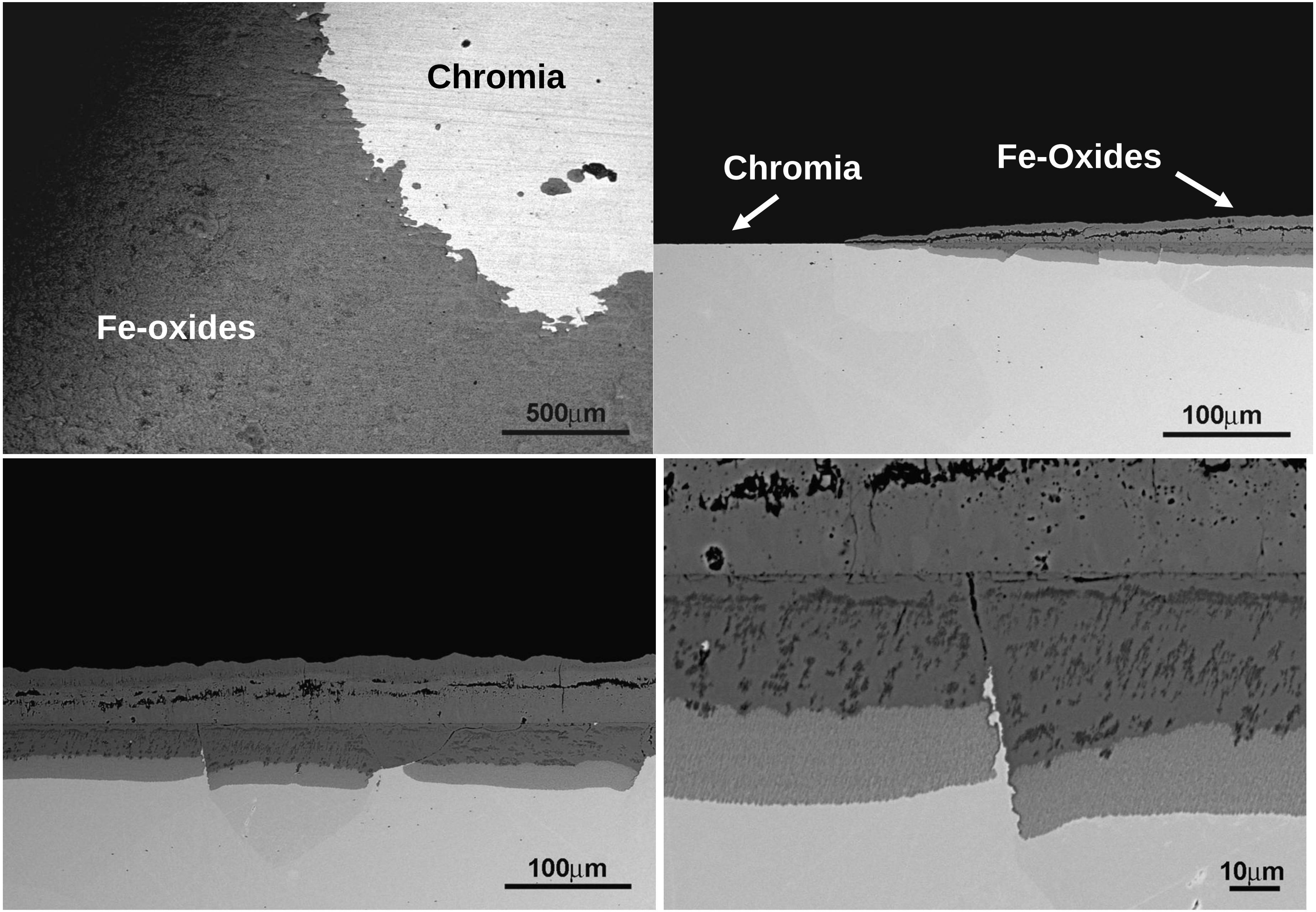

Weight Change (mg/cm²)
0
5
10
15
20
25
Ar+30%H2O
Ar+30%H2O+3% O2
21.03
14.06
1
16.56
13.82
0.1
0.65
13.35
0.09
0.22
0.12
8.97
9.97
0.05
2.92
3.88
0.02
0.08
0.09
0.13
0.51
0.46
0.16
0.01
0.03
0.02
Fe-10Cr
Fe-..
Fe-22Cr
Fe-..
T91
T92
Ni-22Cr
Fe-..
IN617

Isothermal Oxidation of Fe-22Cr at 650°C in Ar+30%H_2O+3%O_2



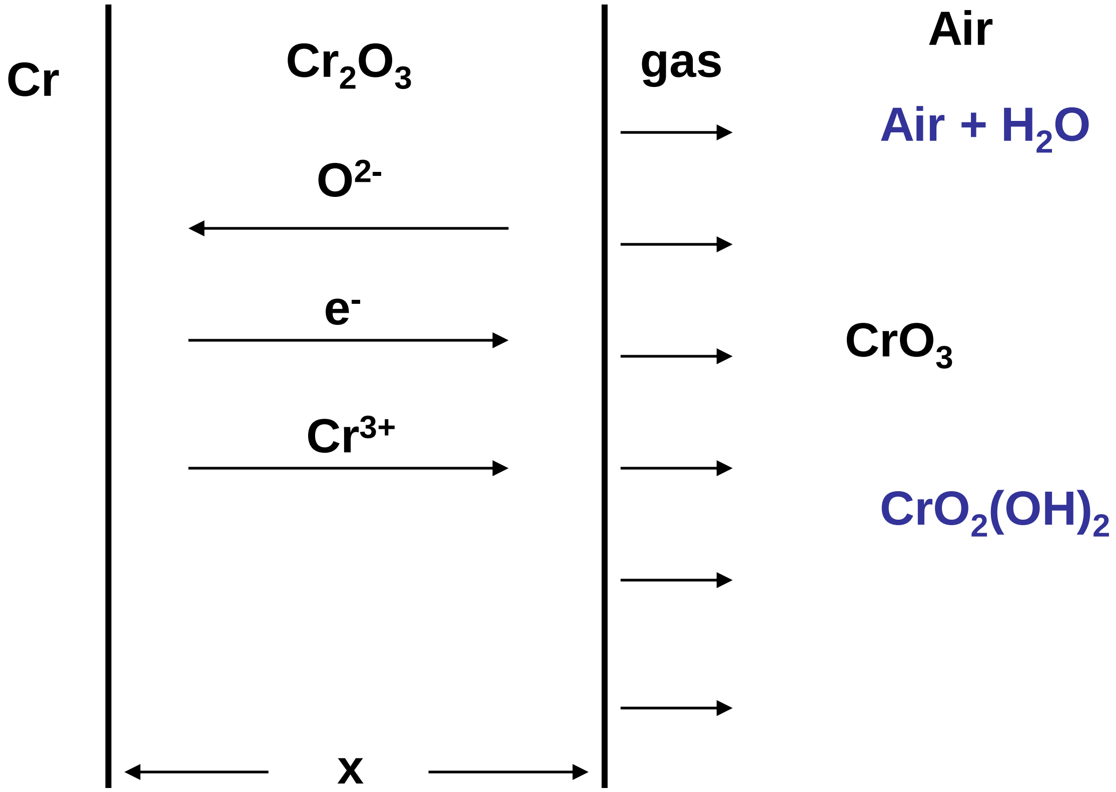
Results for Fe-22Cr

96hrs@650°C in Ar-30%H_2O-3%O_2



Effect of Water Vapor on Chromia Evaporation

Oxide Growth and Vaporization



Cr

Cr_2O_3

O^{2-}

e^-

Cr^{3+}

gas

Air

Air + H_2O

CrO_3

$CrO_2(OH)_2$

x

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) = 2CrO_3(g)$$

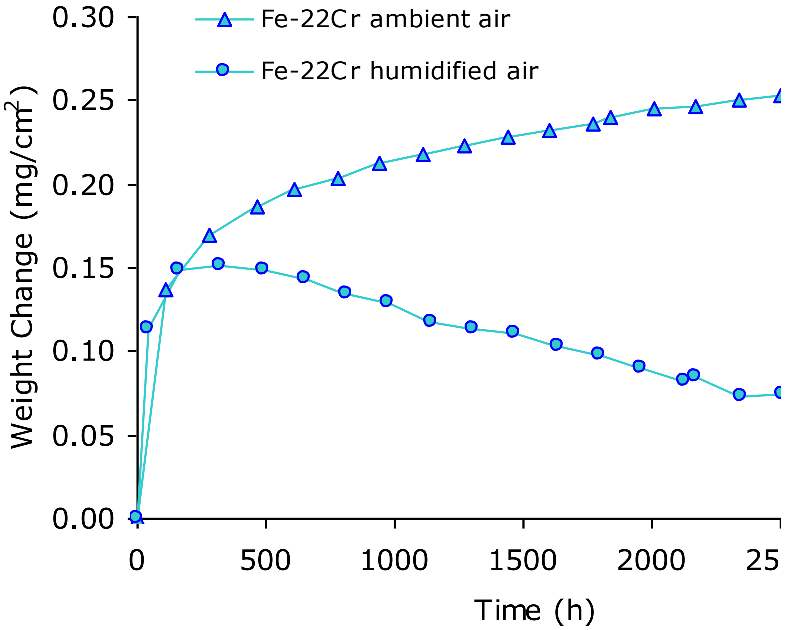
C. S. Tedmon, *J. Electrochem. Soc.*, 113, 766 (1966).

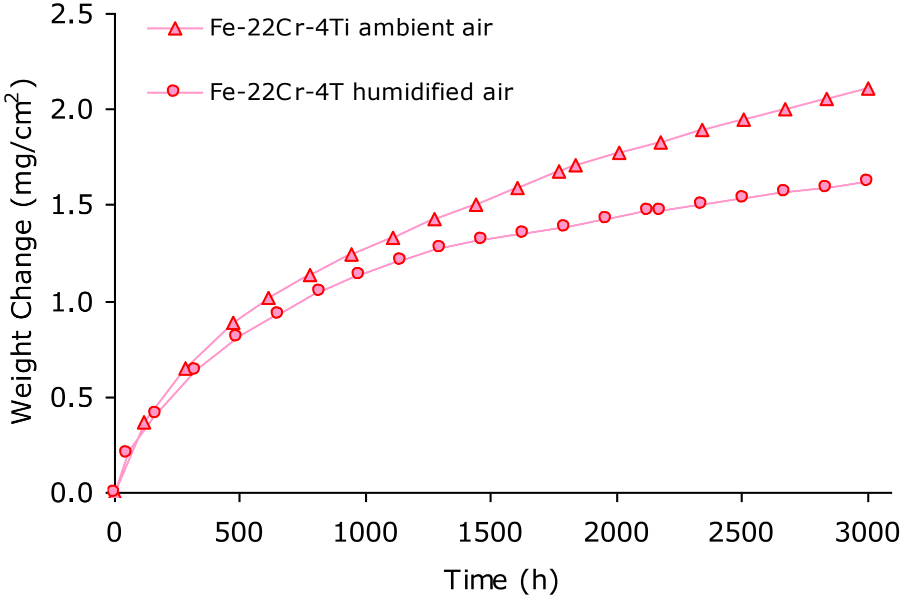
Composition of Ferritic Alloys Fabricated at ATI-Allegheny Ludlum

Heat Identification Code

Element	**RV 2103**	**RV 2104**	**RV 2095**	**RV 2096**	**RV 2097**
Cr	21.8	21.8	22.1	22.2	22.2
Ti	0.004	0.84	1.65	2.72	3.98
Mn	0.033	0.030	0.031	0.024	0.023
C	0.010	0.013	0.010	0.016	0.017
N	0.018	0.018	0.011	0.008	0.008
Ce	0.004	0.027	0.031	0.027	0.027
La	0.001	0.009	0.012	0.012	0.010
Al	0.005	0.005	0.008	0.030	0.049
Si	0.043	0.042	0.036	0.020	0.020

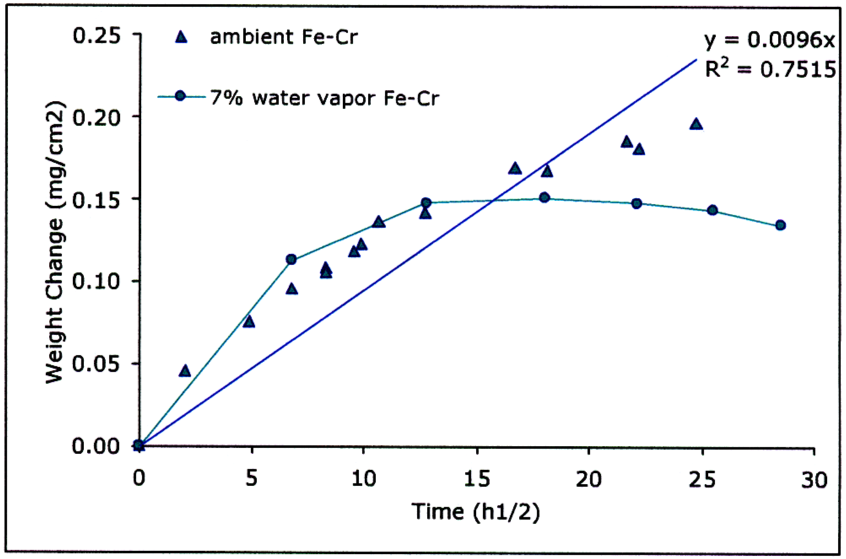
Fe – 22 Cr ± Ti at 760ºC



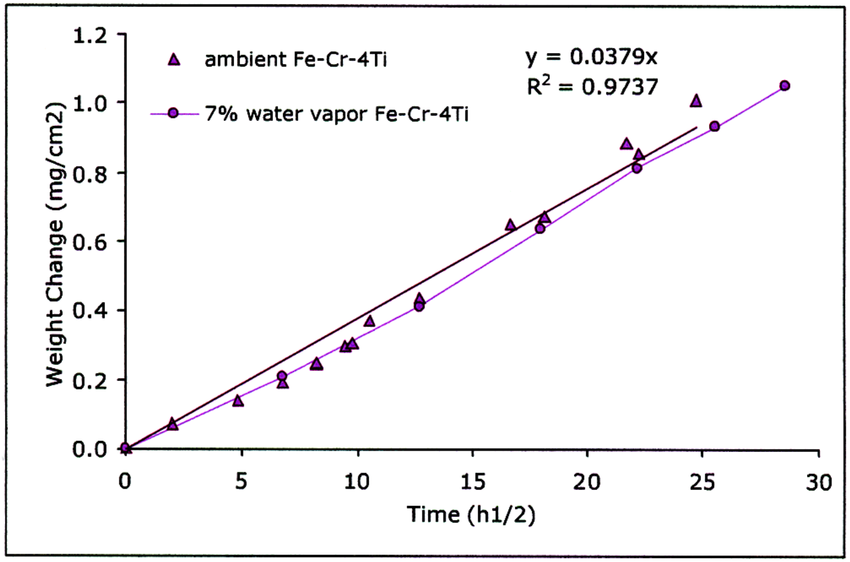


Ti Effects on Oxidation

760°C

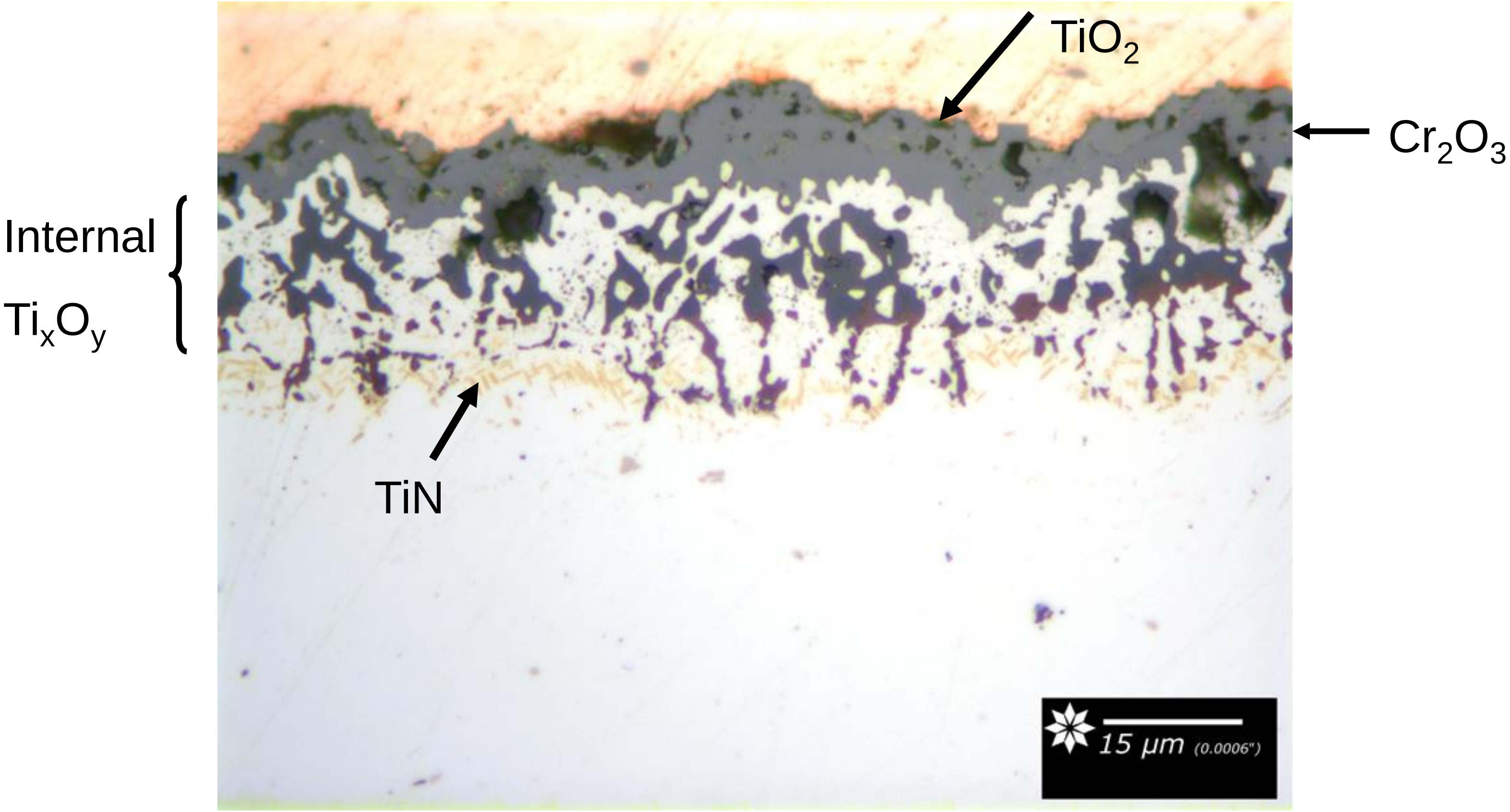


Fe-22Cr



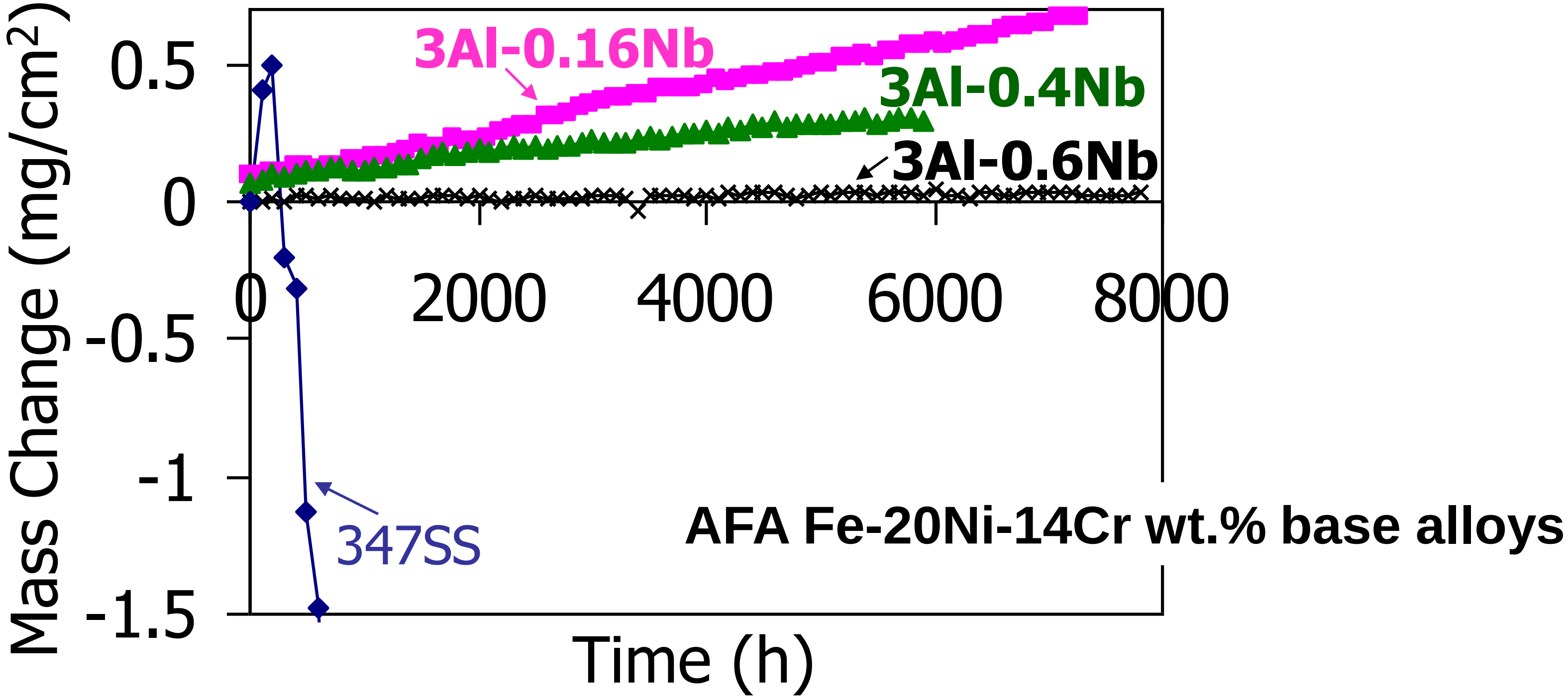
Fe-22Cr-4Ti

Fe-Cr-4Ti Exposed 500 h at 816^{o}C in air



Higher Nb in AFA Alloy Favors Better Oxidation Resistance in Air + Water Vapor

Oxidation at 650°C in Air + 10% Water Vapor



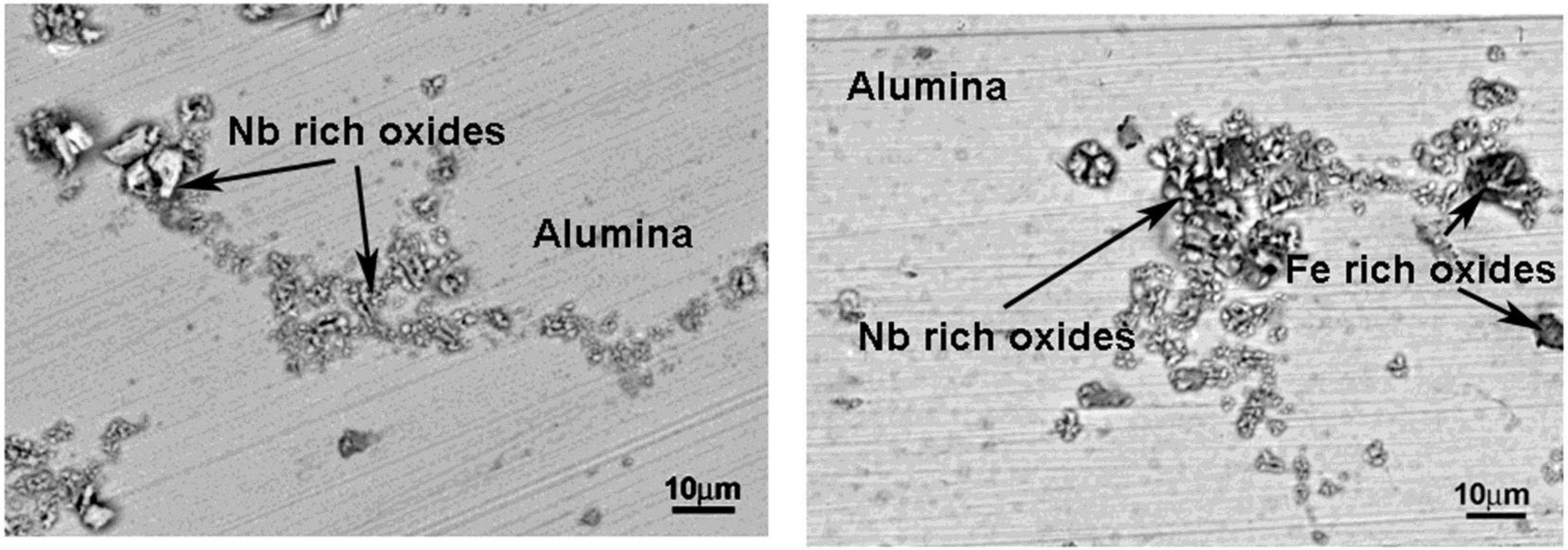
- Excellent resistance to ~8000 h of exposure
- 347 stainless steel shows accelerated attack after a few hundred hours

M. P. Brady et al, Oxidation of Metals, 72, 311 (2009).

Preliminary Results with Alumina-Forming Austenitic (AFA)Steels

Chemical composition of AFA steel OC4 (wt.%)

Fe	Ni	Cr	Al	Nb	Mo	Mn	W	Cu	Si	C	V	Ti	B	N	Co	S	P
bal.	25	14.02	3.52	2.54	2.01	1.99	0.99	0.51	0.16	0.111	0.05	0.05	0.0087	0.001	<0.01	0.001	<.005



250hrs@650°C in Air

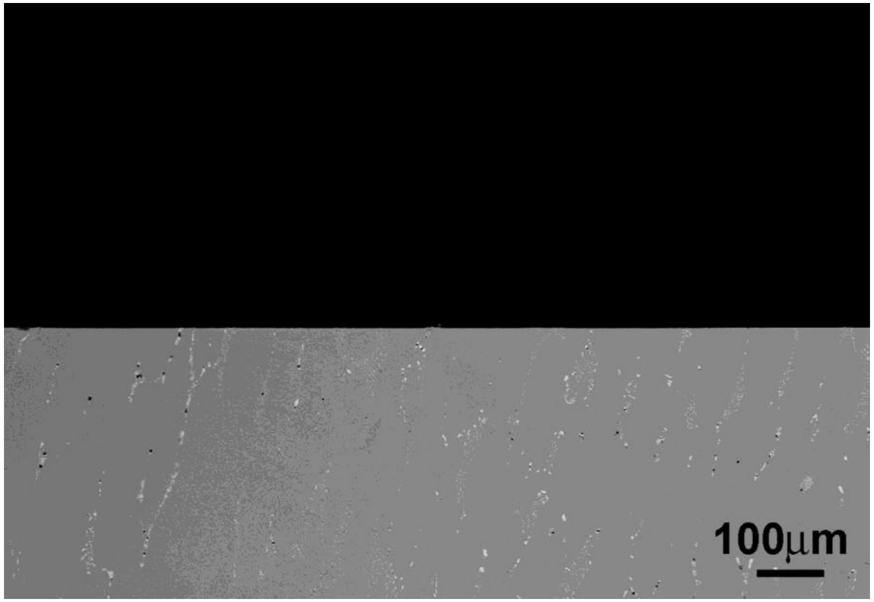
96hrs@650°C in Ar-30%H_2O-3%O_2

Surface Images

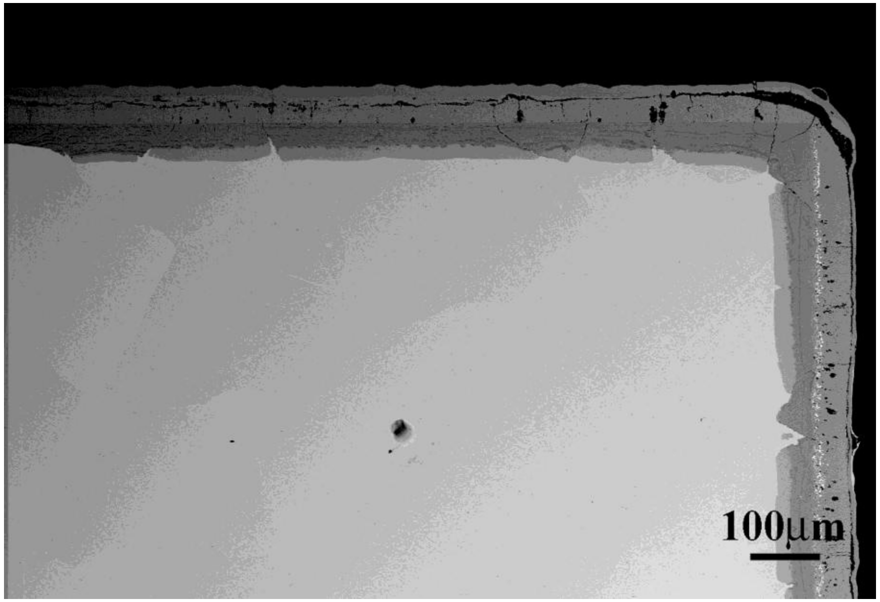
Alumina Forming Austenitic (AFA) Steel vs Fe-22Cr

96hrs@650°C in Ar-30%H_2O-3%O_2

Alumina Forming Austenitic (AFA) Steel

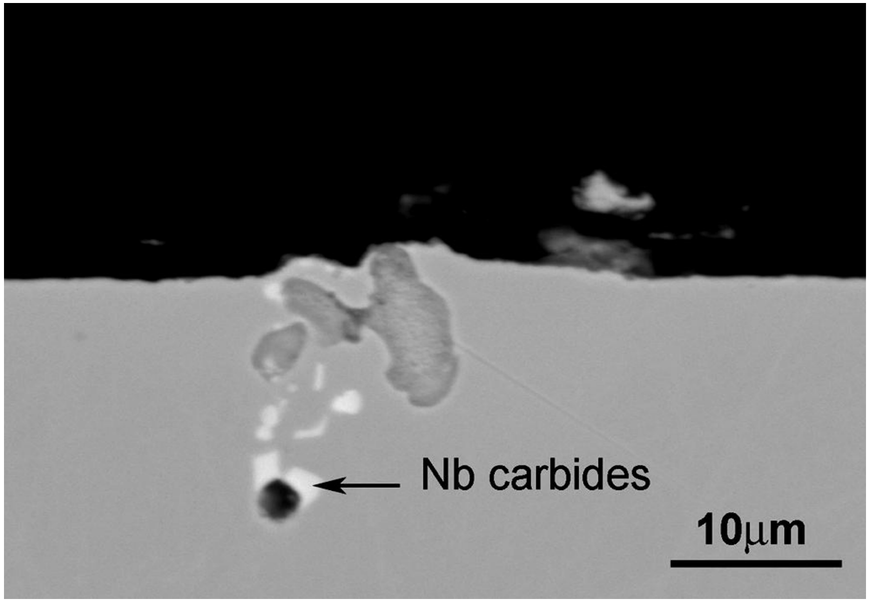


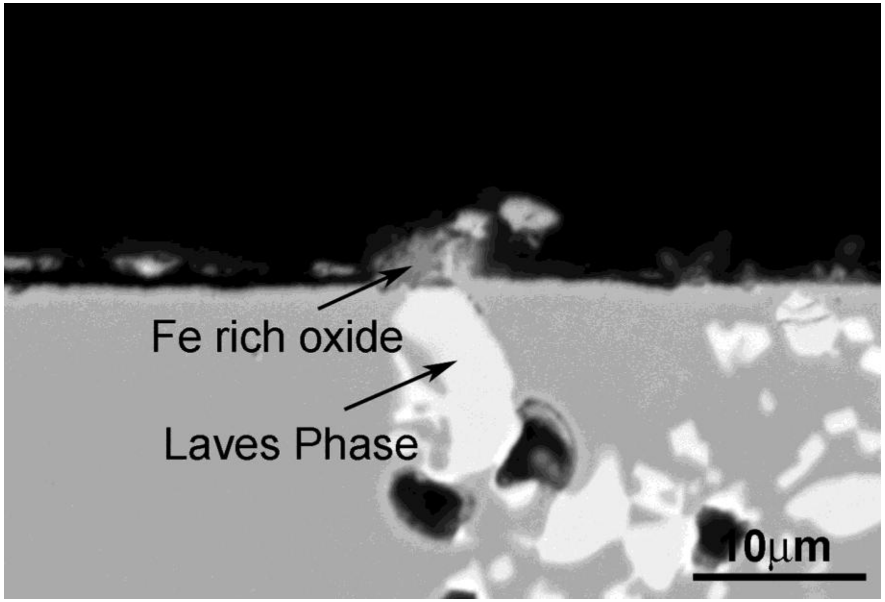
Fe-22Cr



Alumina Forming Austenitic (AFA) Steel OC4

96hrs@650°C in Ar-30%H_2O-3%O_2



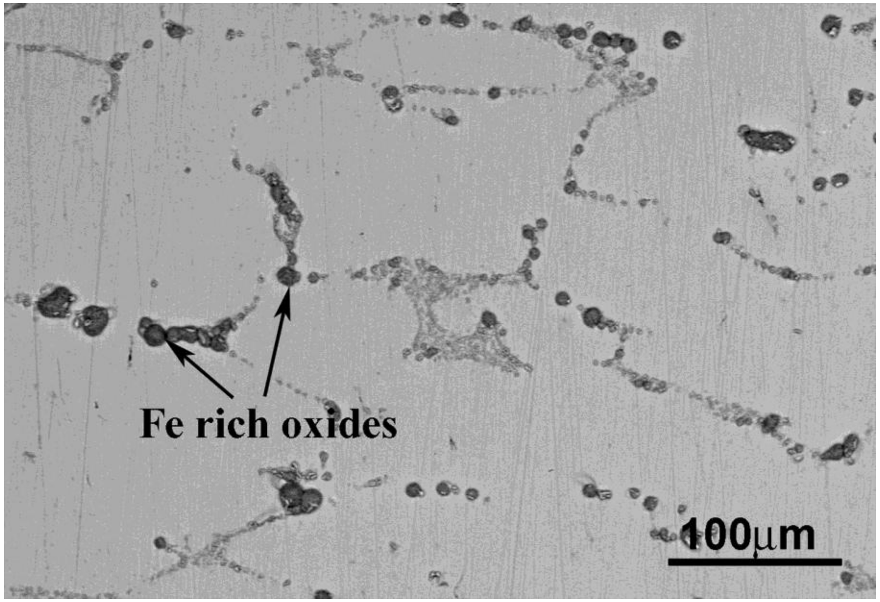


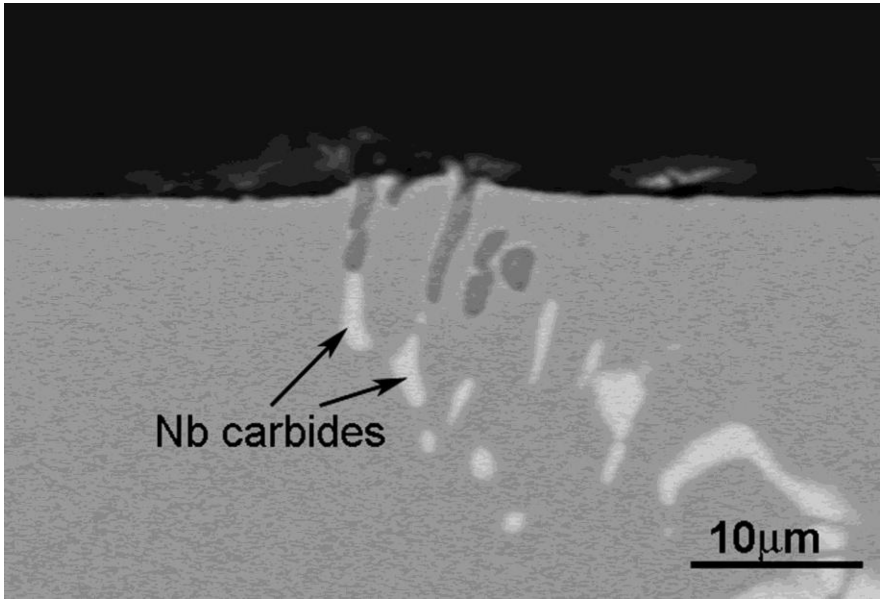
Alumina Forming Austenitic (AFA) Steel
OC5

Chemical composition of AFA steel OC5 (wt.%)

Fe	Ni	Cr	Al	Nb	Mo	Mn	W	Cu	Si	C	V	Ti	B	N	Co	S	P
bal.	25	14.02	3.00	1.00	2.01	1.99	0.99	0.51	0.16	0.111	0.05	0.05	0.0087	0.001	<0.01	0.001	<.005

96hrs@650°C in Ar-30%H_2O-3%O_2





Concluding Remarks

- Water vapor disrupts the selective oxidation of Cr.

  At high T (900^{o}C) it accelerates internal oxidation.

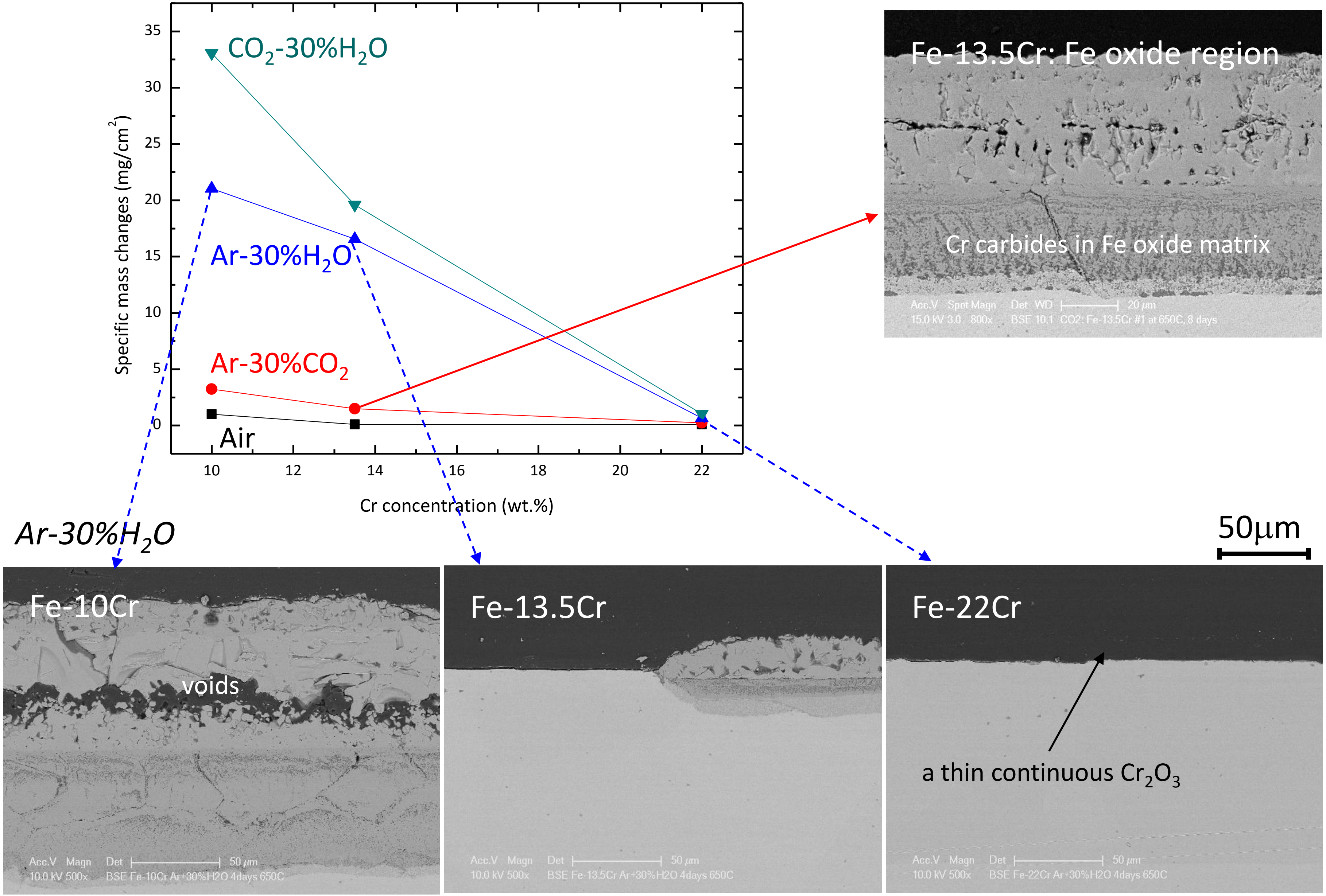
  At low T (650^{o}C) it accelerates chromia growth.
- Excess oxygen exacerbates the negative effects of water vapor. (Enhanced chromia evaporation.)
- Minor alloying elements, e. g. Ti, can improve the resistance of chromia-formers.
- Alumina-forming austenitic steels are substantially more resistant to water vapor than are chromia-formers.
- Carbon dioxide disrupts the selective oxidation of Cr by injecting carbon into the alloy, which precipitates subsurface Cr-carbides.
- Excess oxygen diminishes the negative effects of carbon dioxide.

Acknowledgements

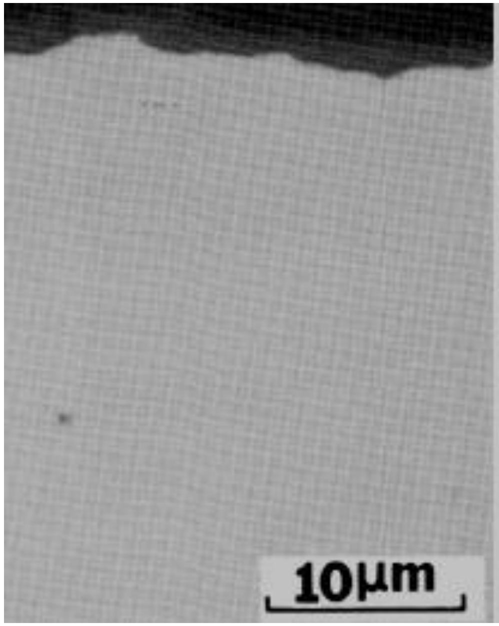
The work at University of Pittsburgh was performed in support of the National Energy Technology Laboratory's ongoing research on Advanced Combustion under RES contract DE-FE0004000. The authors are most grateful to Prof. Shigenari Hayashi for help with the GD-OES measurements and Dr. M. P. Brady at ORNL for providing the AFA alloys.

DISCLAIMER

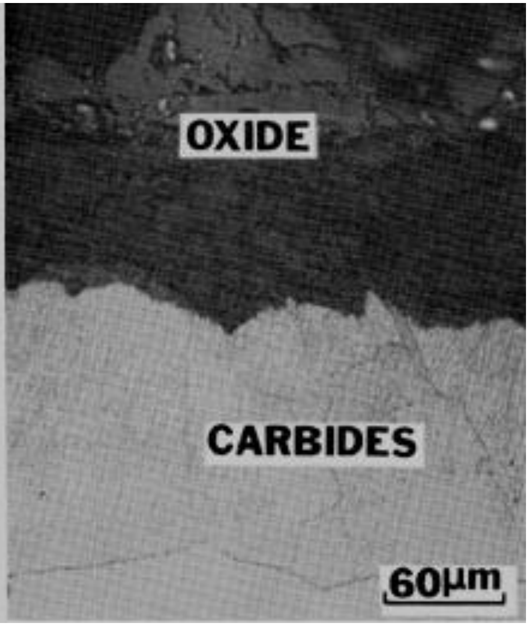
Fe-Cr binary model alloys at 650°C
: Effects of Cr concentration and atmosphere



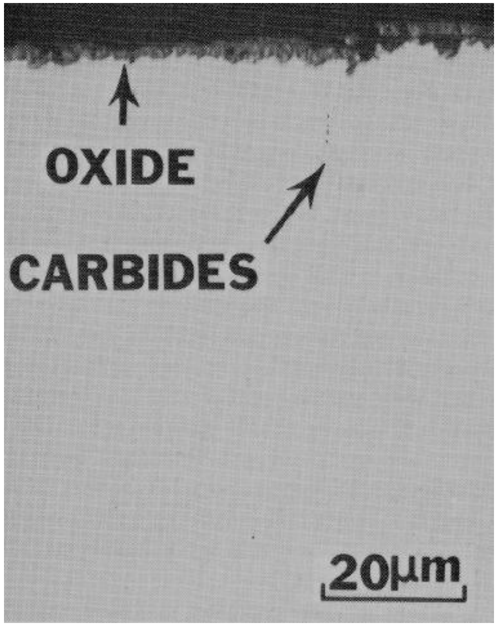
Effects of CO_2 and Cr Contents on Degradation of Fe-Cr Alloys at 900°C



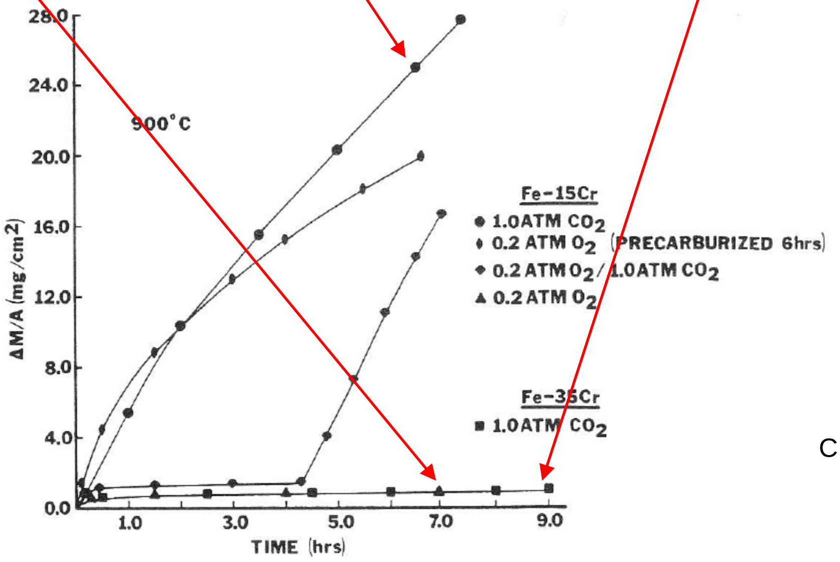
Fe-15Cr in air (16.6h)



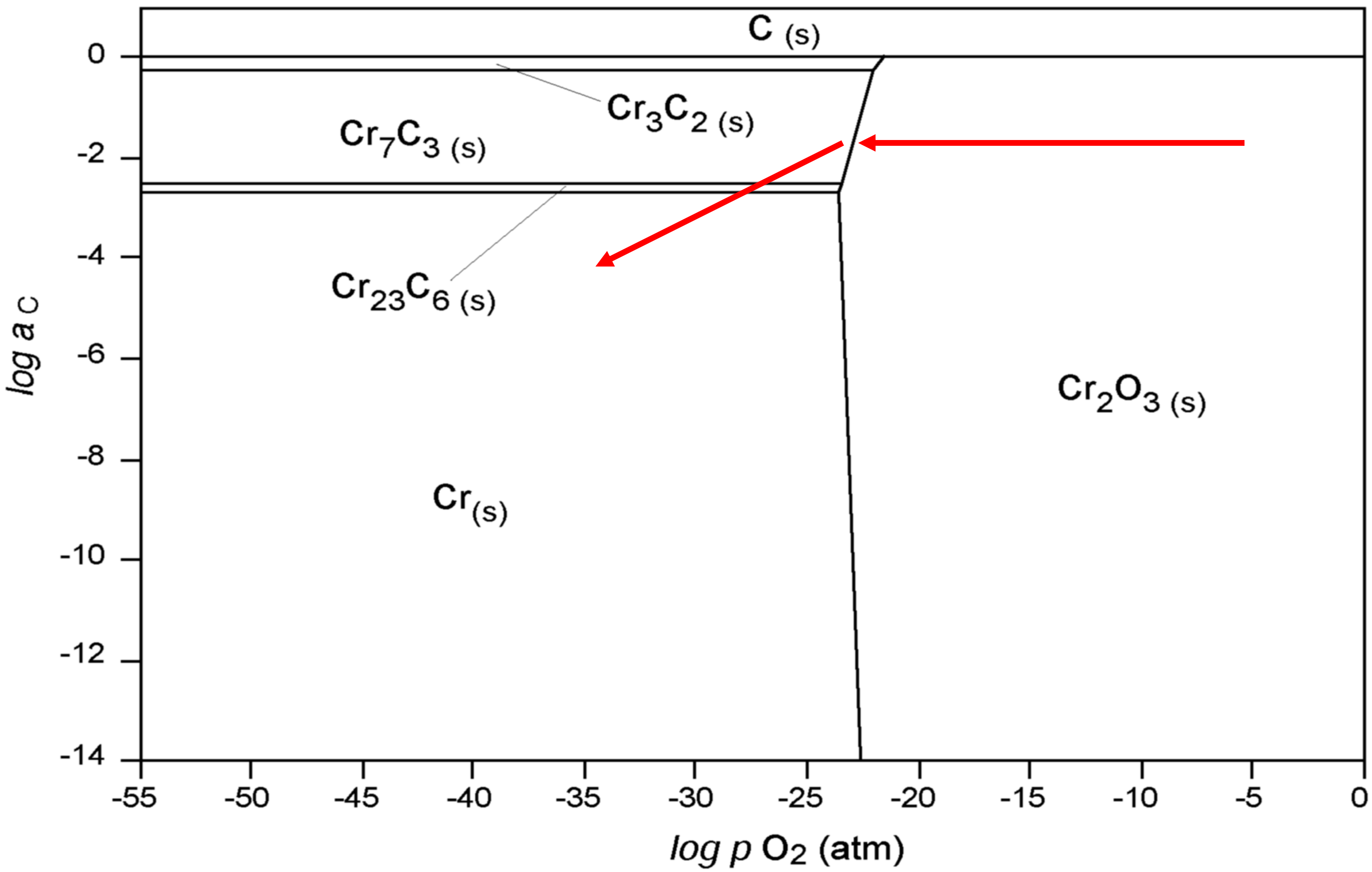
Fe-15Cr in CO_2 (4h)



Fe-35Cr in CO_2 (6.5h)



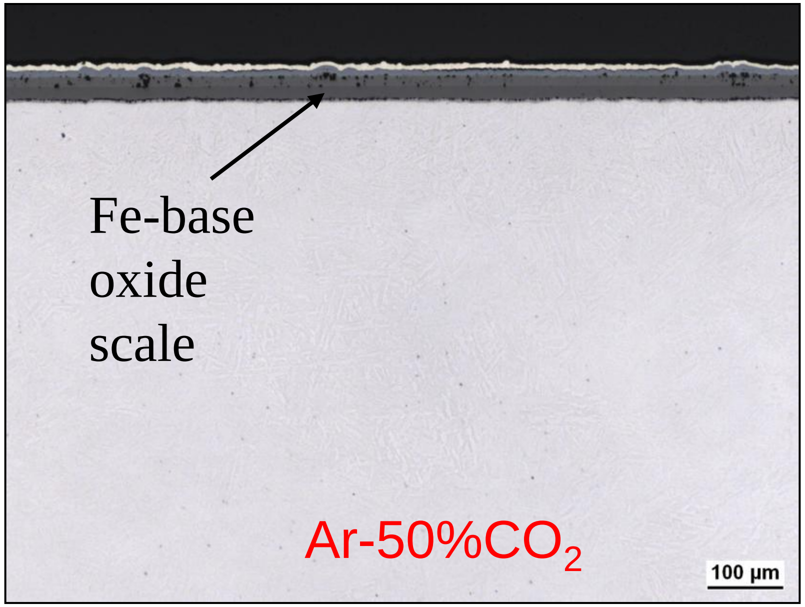
C.S. Giggins, F.S. Pettit, *Oxid. Met.* (1980)

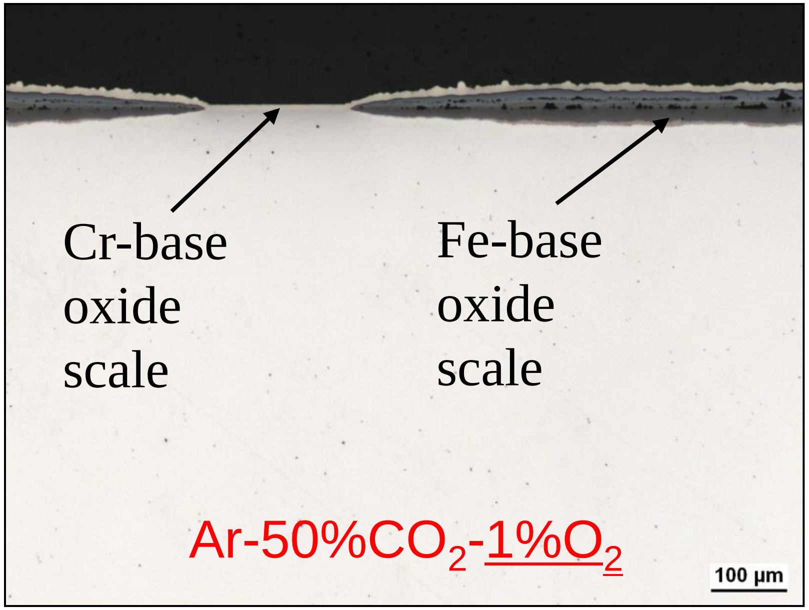


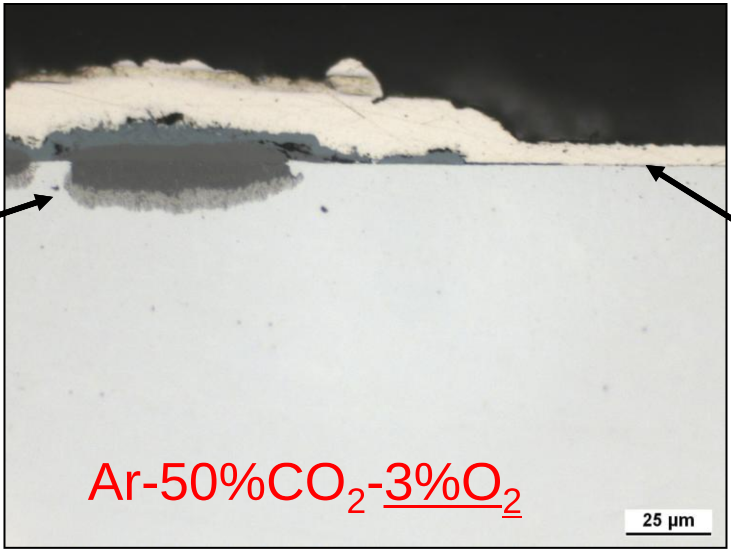
Isothermal Stability Diagram for the Cr-C-O System at 1250K

Effect of Excess Oxygen in CO_2 Exposures

Cross sections of 9%Cr steel P92 after 1000h exposure at 550°C







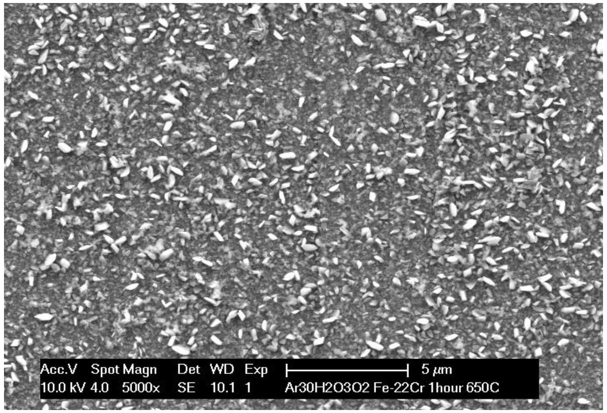
Effect of CO_2 On Selective Oxidation of Cr

$$N_{Cr}^{(1)} > \left[\frac{\pi g^{*}}{3} N_{O}^{(S)} \frac{D_{O} V_{m}}{\tilde{D}_{Fe-Cr} V_{CrO_{1.5}}} \right]^{1/2} + N_{Cr}(\text{Carbide})$$

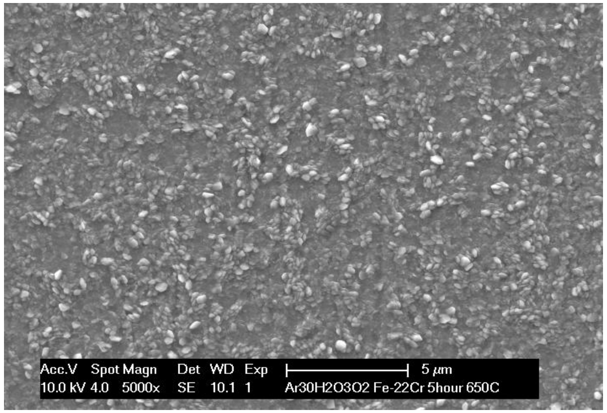
$$\mathbf{CO_2(g) = \underset{\underset{O_2(g)}{\uparrow}}{O}(Ox) + CO(g)}$$

The presence of excess O_2 provides a source of oxygen in addition to the CO_2 molecules and decreases $N_{Cr(}$(Carbide).

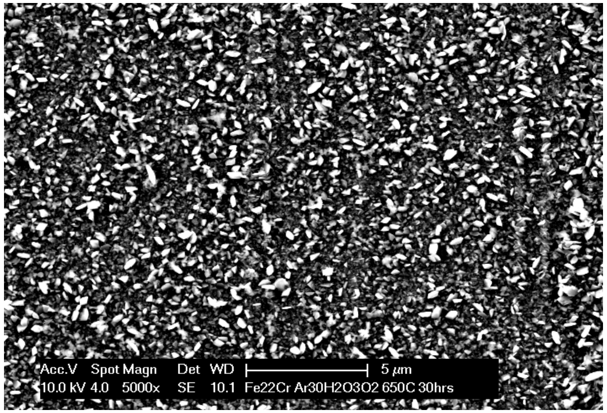
Characterization of Fe-22Cr Oxidized in Ar+30%H_2O+3%O_2 at 650°C



1hr

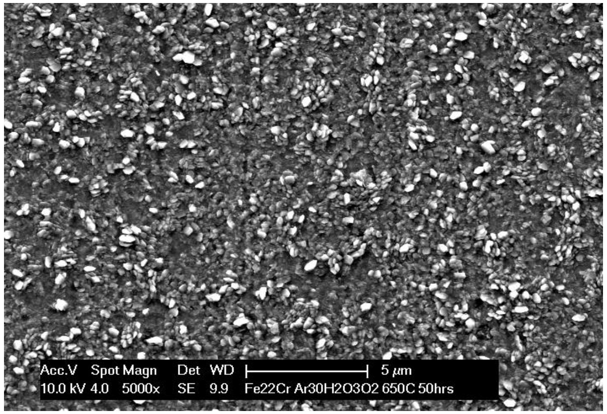


5hrs

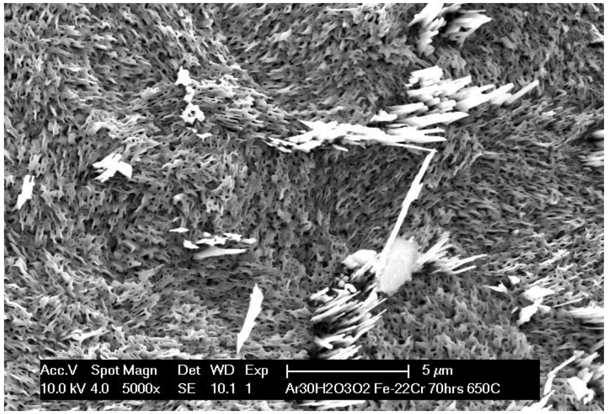


30hrs

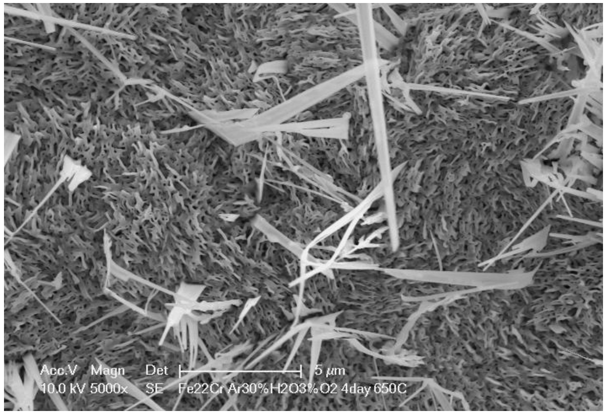
XRD analysis	Cr_2O_3	$Cr_2O_3 + Fe_2O_3$	$Cr_2O_3 + Fe_2O_3$



50hrs



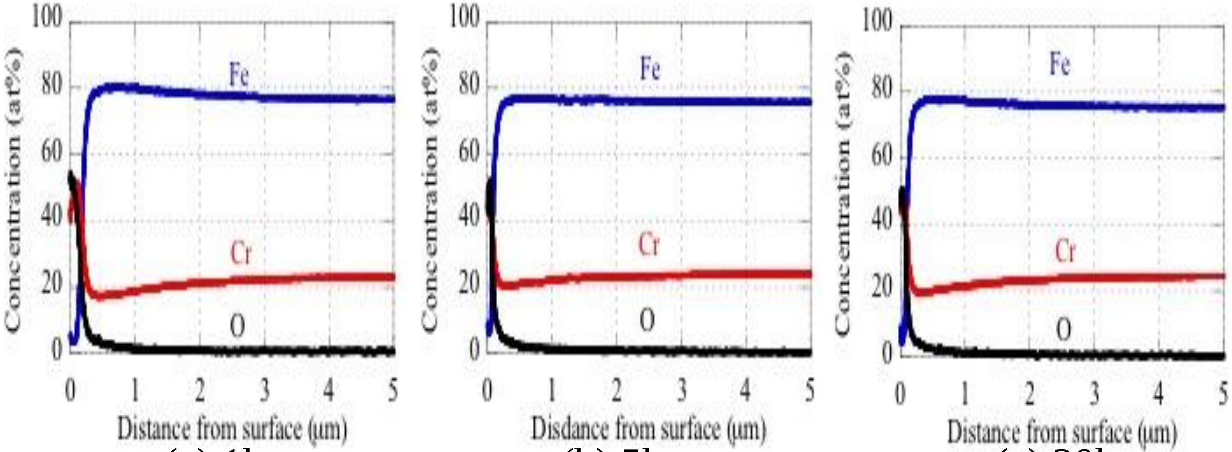
70hrs



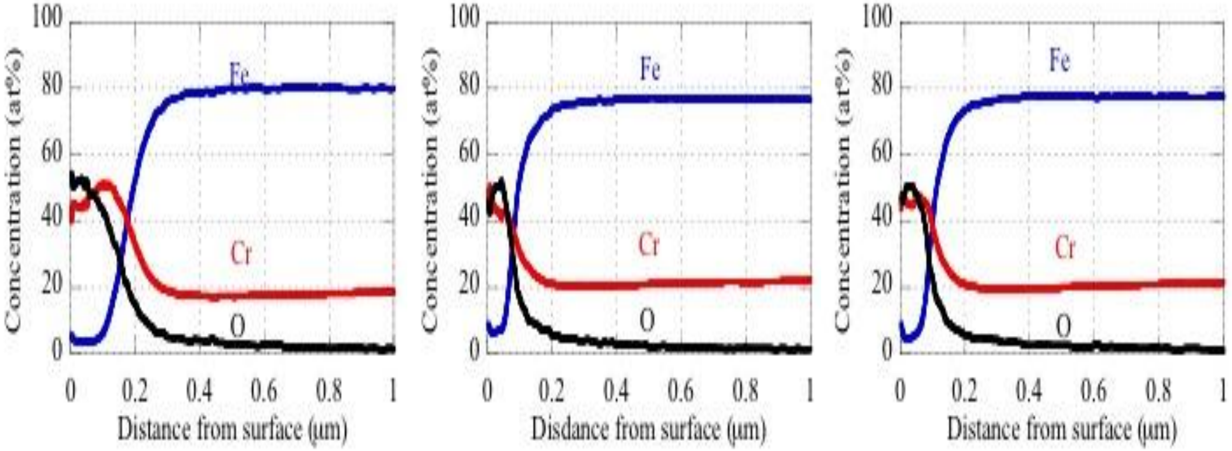
96hrs

XRD analysis	Fe_2O_3	Fe_2O_3	Fe_2O_3

GD-OES of Fe-22Cr Oxidized in Ar+30%H_2O+3%O_2 at 650°C



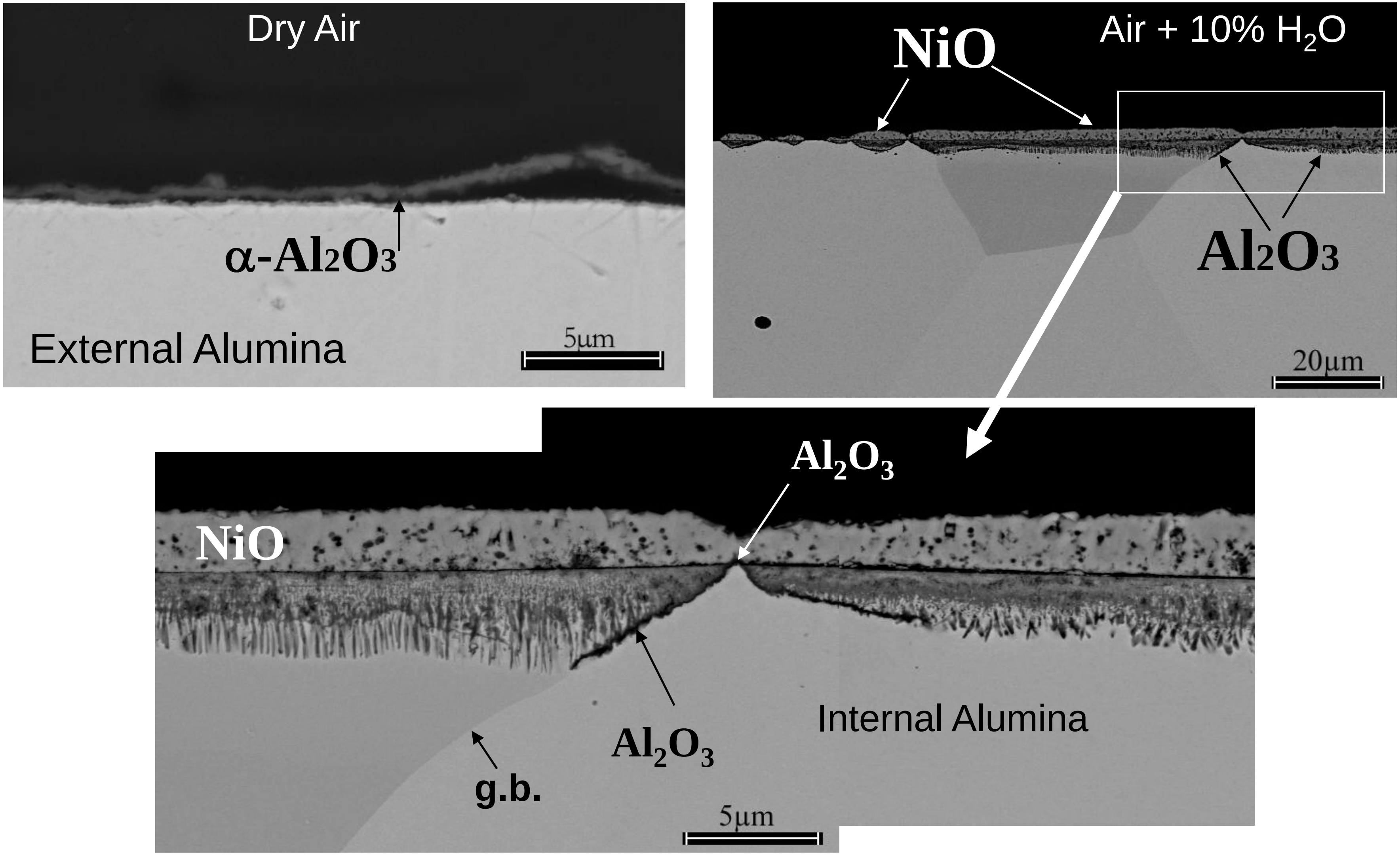
(a) 1hr (b) 5hrs (c) 30hrs



(d) 1hr (e) 5hrs (f) 30hrs

Effect of H_2O On Selective Oxidation

Ni-Cr-Al oxidized @ 1100°C

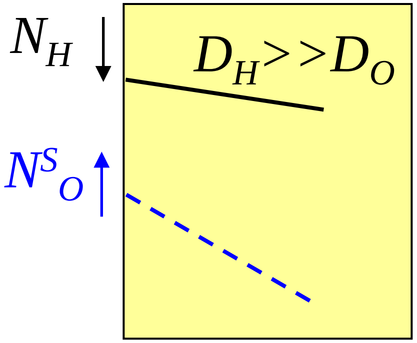


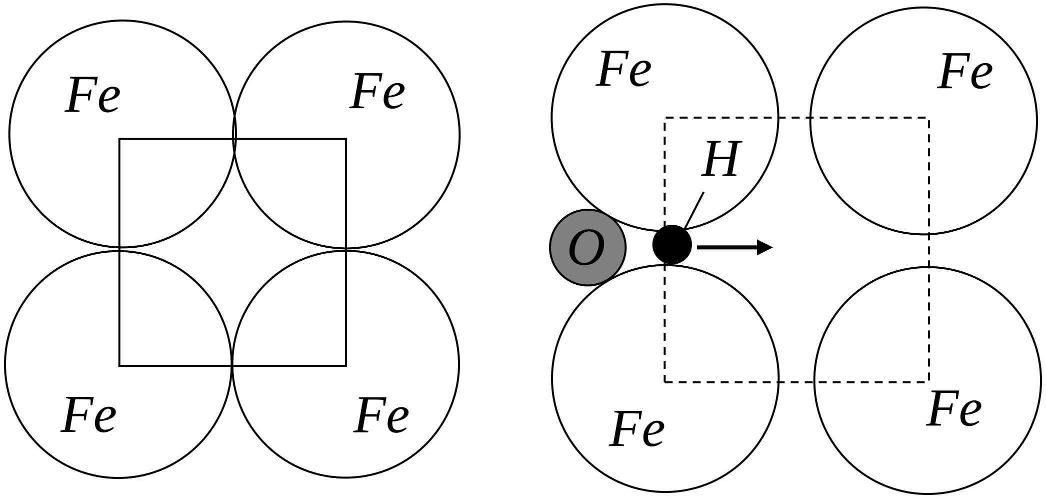
Proposed mechanism of enhanced internal oxidation of Cr in $(H_2)H_2O$-containing gases

$$N_{Cr}^{(1)} > \left[\frac{\pi g^{*}}{3} N_{O}^{(S)} \frac{D_O V_m}{\tilde{D}_{Fe-Cr} V_{CrO_{1.5}}}\right]^{1/2}$$

$$H_2O(g) = 2\underline{H} + \underline{O}$$

$$N_O^S = K_1 \frac{p_{H_2O}}{N_H^2}$$





Hydrogen increases oxygen solubility and/or diffusivity in metal