The Growing Importance of Oxide Growth and Exfoliation (OGE) for HRSGs

Earlier versions presented at EHF2019 and ABHUG 2019

Barry Dooley

HRSG Forum (HF2021)
Virtual Event
2^{nd} June 2021

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Outline of Topics

1. Introduction to Problems Emanating Directly from OGE since 1960s

2. Introductions to the Oxides that Grow in Steam and the Generation of Stresses leading to Exfoliation

3. The Unique Classifications/Indices for OGE on Ferritic and Austenitic alloys - OGEI

4. Brief mention of the Effects of Cycle Chemistry including FFS

5. Examples of the use of the Data Bases/Indices to identify deposit, erosion and other damage mechanisms around the cycle

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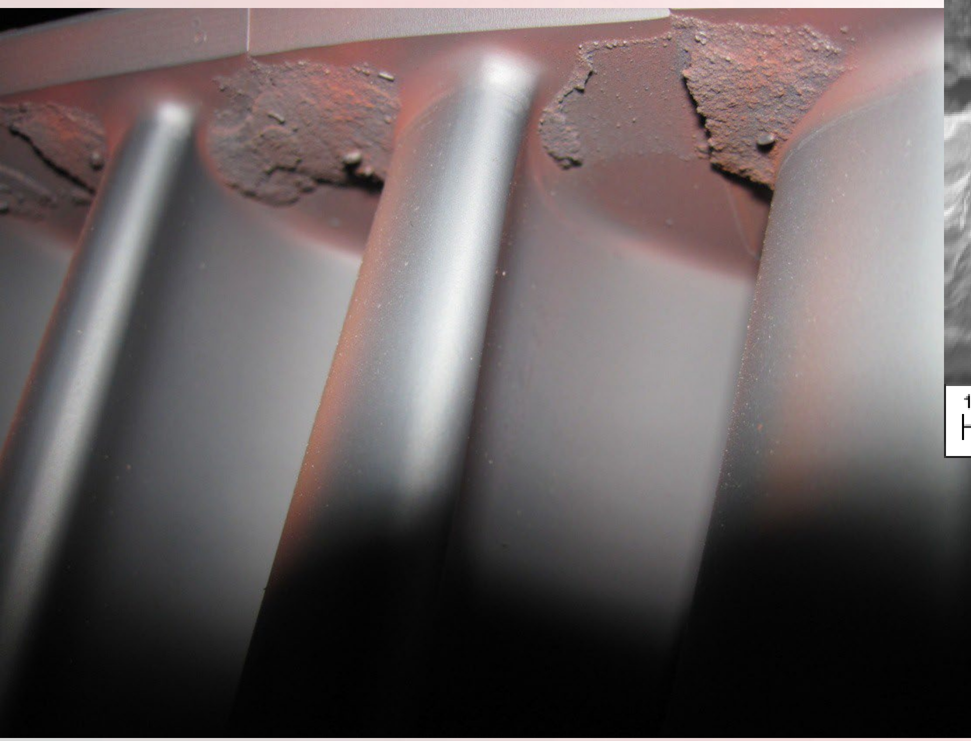
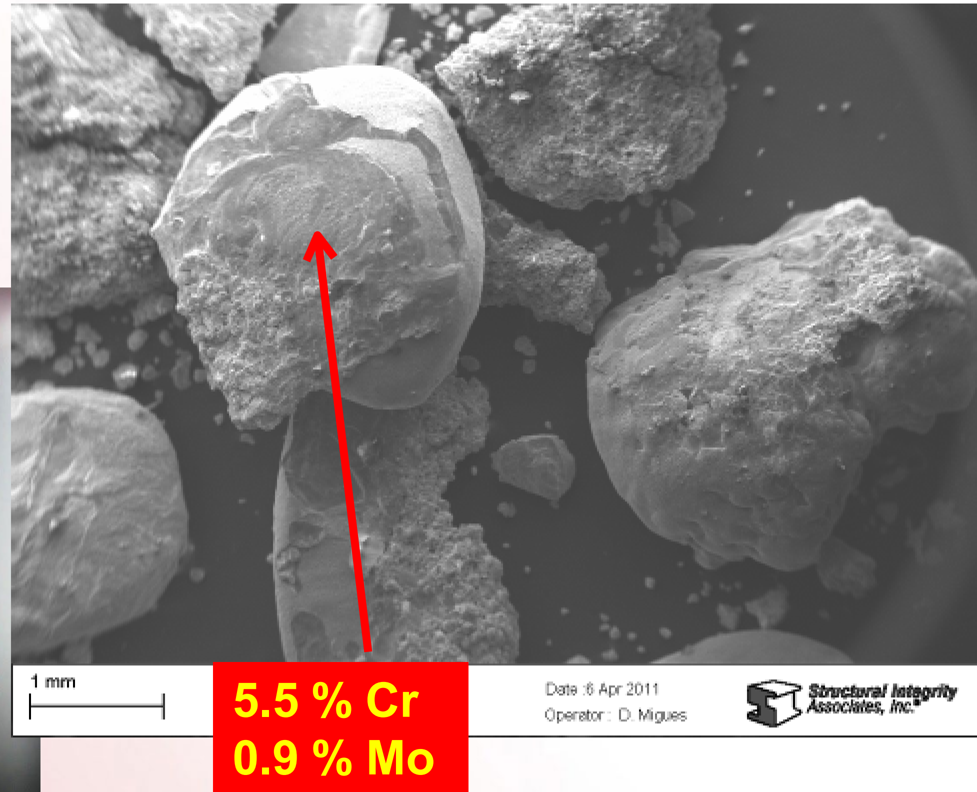
OGE has been an Enormous Problem in Conventional Fossil Plants since the late 1960s

Oxide Growth and Exfoliation (OGE) Causing Valve Erosion, Blockage and Sticking

Performance and Capacity Losses due to Turbine Deposits

Reheater materials: T23, T/P 91





SH/RH Materials & Environments

Ferritic Materials (fossil & combined cycle plants)

- T11, T22, T5, T9, T23, T91

Austenitic Materials (mainly fossil plants)

- TP304H, TP316H, TP 321H, TP347H, Fine Grained (TP347HFG), S304H and other shot peened

Environments

- Saturated and Superheated Steam
- Oxygen levels range from 1 – 400+ ppb
- GT EGT (7FA – 7HA) 590 - 620 ^{o}C (1100 - 1150^{o}F)
- Duct burners
- Tube Temperatures range up to 650^{o}C (1200^{o}F)

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The Three Steam Grown Oxides of Importance:
Magnetite Fe_3O_4
Iron/Chromium Spinel $(Fe,Cr,Ni)_3O_4$
Hematite Fe_2O_3
are semiconductors and grow by counter flux ionic diffusion processes of Fe^{2+} moving outwards and O^{2-} (oxide ion) moving inwards.

Superheated steam with temperatures up to 600C +
Mechanism is covered in Dooley/Wright papers

Wright/Dooley, Materials at High Temperatures, 2011
Dooley/Wright, PPChem 2019

Coefficients of Thermal Expansion (CTE) of Materials and Oxides

	CTE ($K^{-1}x10^{-6}$) [Armitt 1978]		CTE ($K^{-1}x10^{-6}$) [Holcomb 2019]	
	300°C	600°C	300°C	600°C
T22 Ferritic	14.0	16.2	12.9	13.7
T91 Ferritic	—	—	12.2	12.4
300-series Austenitic	18.6[a]	19.5[a]	17.5[b]	18.7[b]
Magnetite	14.25	16.5	10.4±1.3	13.4±1.4
Hematite	11.9	12.9	10.0	11.8

Extracted from: Dooley/Wright, PPChem 2019

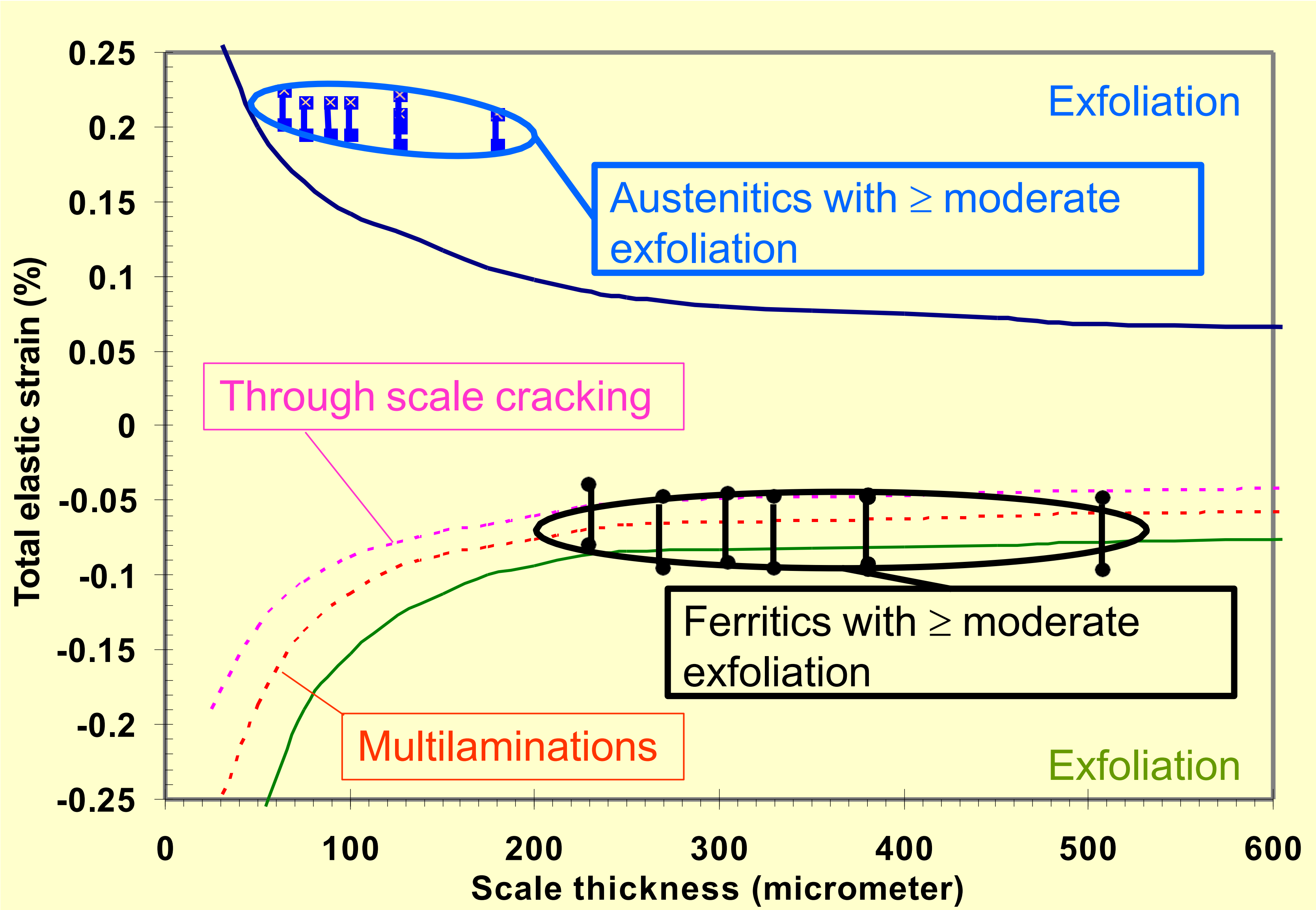
Cooling Strains for Oxides Grown @600°C

	T22 Ferritic	TP316 Austenitic
Scale with 0% Fe_2O_3	-1×10^{-4} Tension	$+1.8 \times 10^{-3}$ Compression
Scale with 20% Fe_2O_3	-0.5×10^{-4} Tension	$+2.0 \times 10^{-3}$ Compression

-ve is tensile, +ve is compressive

Cooling strains are directly related to the magnitude of the temperature drop, not to the rate

Ferritic and Austenitic Oxide Exfoliation Superimposed on Oxide Failure Map



Original Oxide Failure Map: Armitt et al 1978
Exfoliation Data added: Dooley & Paterson, 2003

Oxide Growth on Ferritic Materials in Steam

T11, T12, T22, T5, T9, T91, T23

Morphological Index for Oxide Growth and Exfoliation (OGEI) on Ferritics (For T11, 22, 23 & 91)

1. Initial duplex growth. No laminations. No Fe_2O_3

2. Initiation of inner layers at base of original duplex. Very distinct for T23. Chromium rich bands for T91. As voids form along the oxide/oxide interfaces for T23 and T91 then hematite forms on outside surface.

3. Increasing laminations of equal thickness for T11 and T22, of unequal thickness for T23, increasing chromium-rich bands for T91. Increasing voidage for T23 and T91 leads to increasing hematite on outer magnetite

Examples included on next few slides

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Sources: ABHUG and EHF 2017. Dooley/Wright, PPChem 2019

Morphological Index for Oxide Growth and Exfoliation on Ferritics (OGEI) (For T11, 22, 23 & 91)

4. Initiation of cracks (start of exfoliation). For T11 and 22 cracks initiate perpendicular to M/O. For T91: a) voids grow into delaminations, b) as for T11/22 perpendicular to M/O.

5. Exfoliation. For T11 and 22, thick multi-laminated oxides. Exfoliation with T23 is delamination and has distinct alternate magnetite/spinel layer and is usually large flakes. For T91 is mostly delamination

Examples included on next few slides

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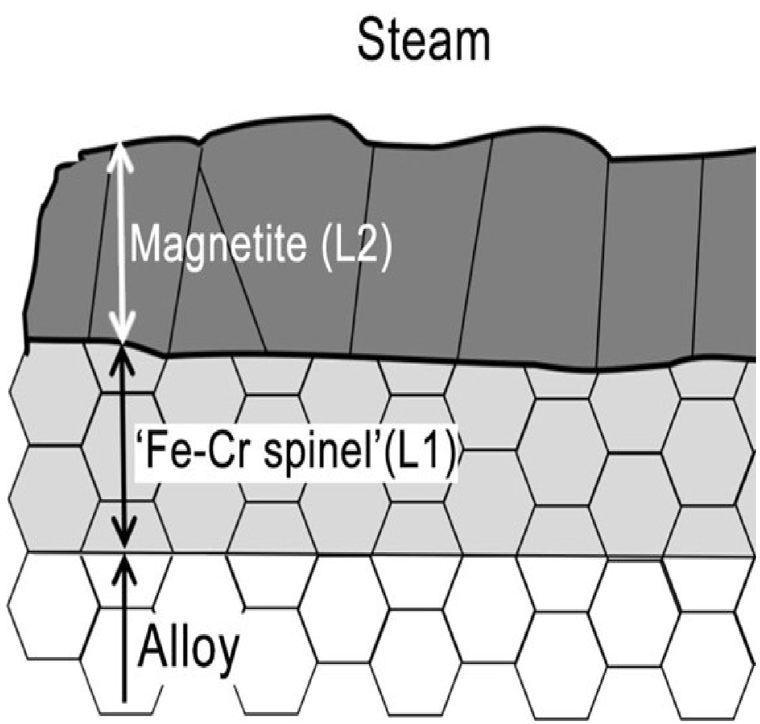
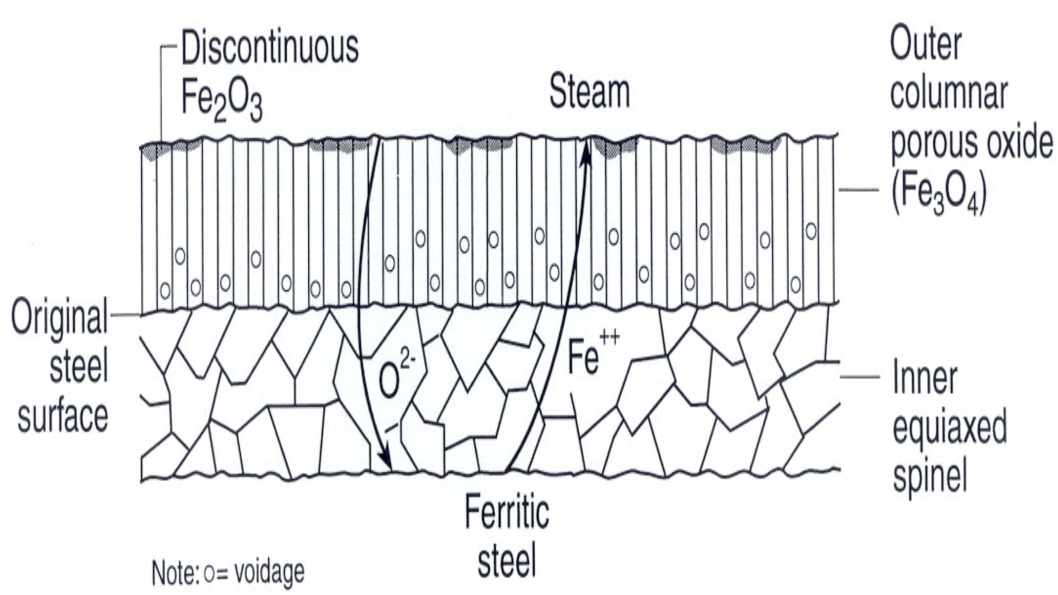
Sources: ABHUG and EHF 2017. Dooley/Wright, PPChem 2019

Initial (Duplex) Oxide Growth on Ferritic Alloys up to 9 wt% Cr

OGEI 1



Dooley/Wright, PPChem 2019



Dooley, Ontario Hydro/CEA. 1979

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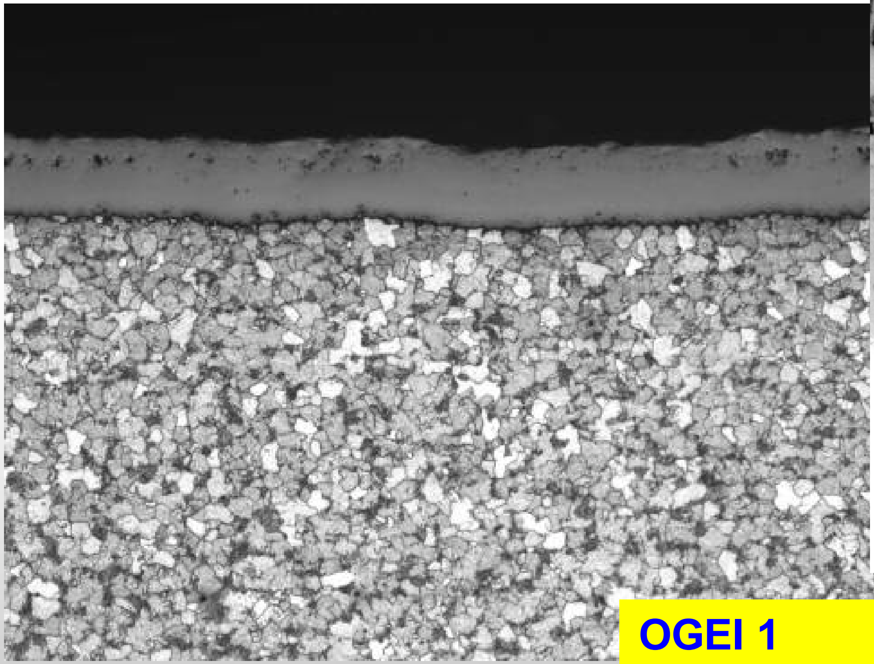
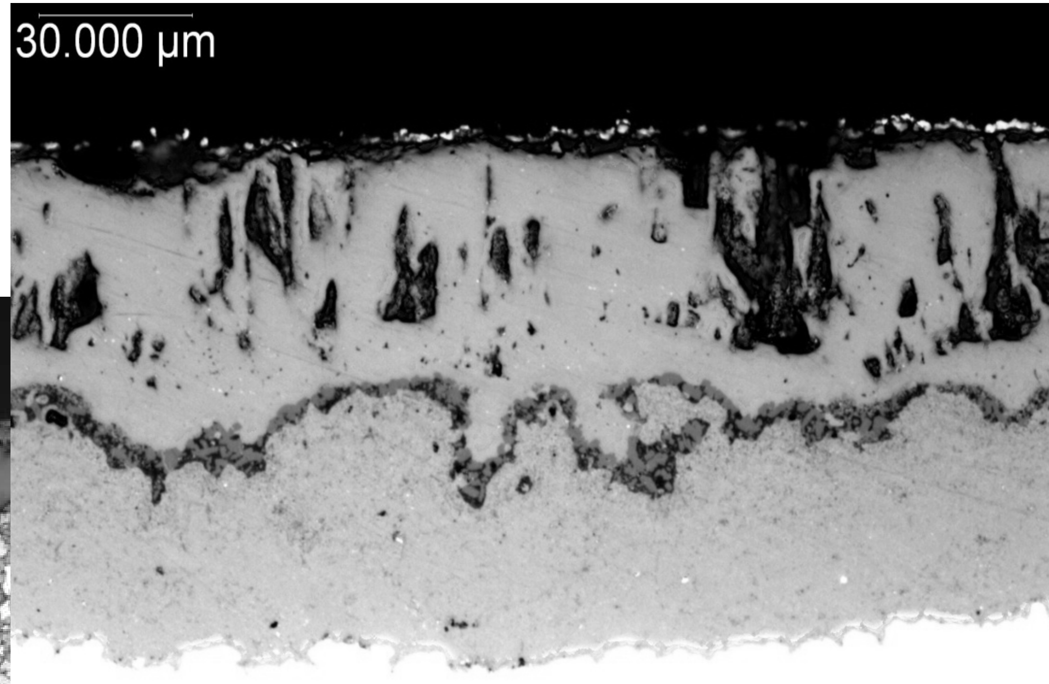
T22 in HRSG RH and Secondary Superheater

158khrs. Steam Temperature 900°F / 480°C

Initially the oxide remains duplex of approximate equal thicknesses (no Fe_2O_3)



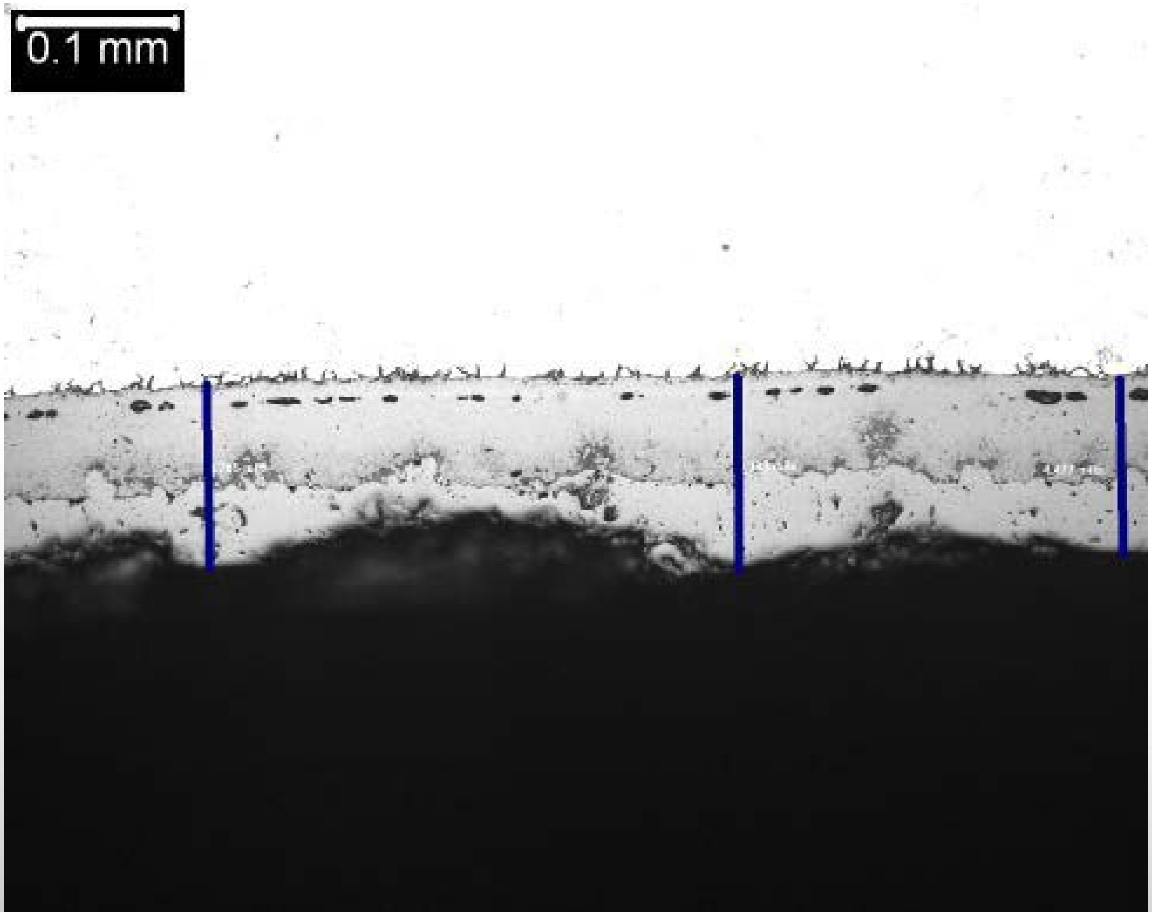
OGEI 1



Canada 2011

T22 in Secondary Superheater (Steam 1000°F / 540°C)

149 khrs, 3120 starts at estimated temperature 980°F/ 526°C



But at some stage it starts to form a new duplex pair (laminate) at the tube/oxide interface

OGEI 2

China 2008

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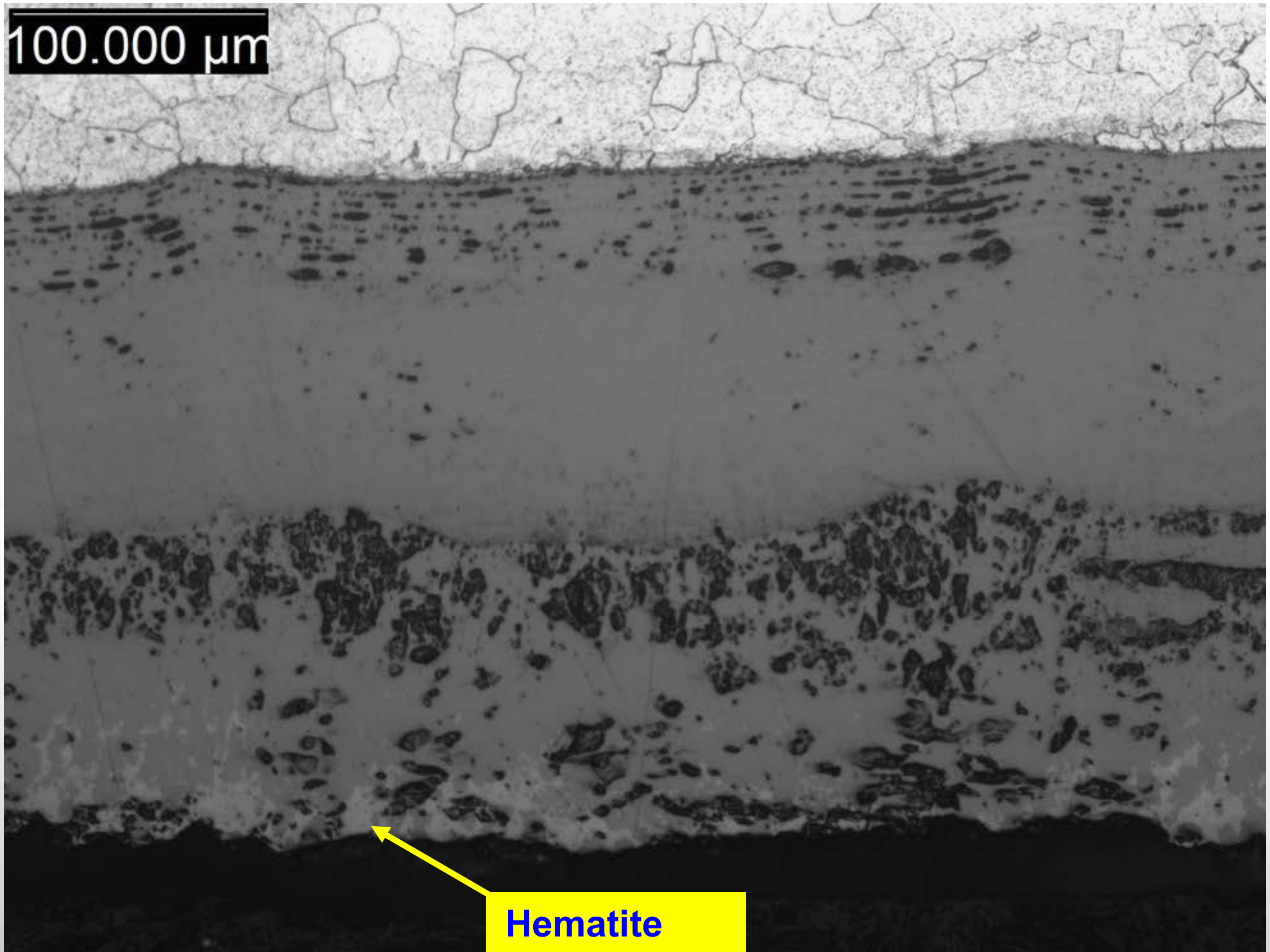
T22 in HRSG Reheater (Steam 565°C, 73,000 hrs)



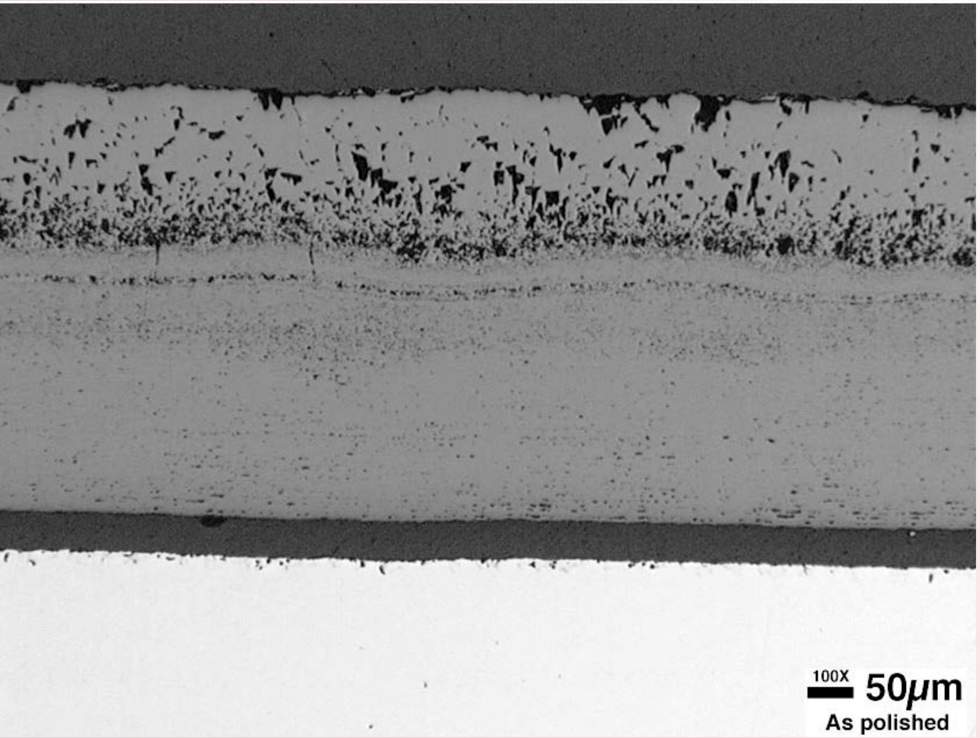
Laminations continue at the tube/oxide interface

OGEI 3

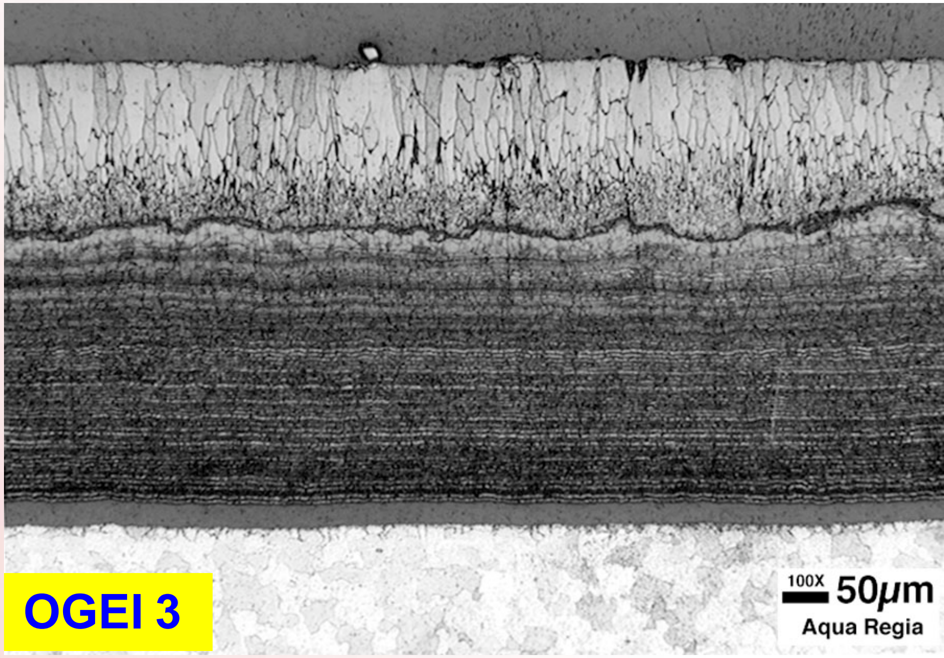
Spain 2016

T22 in SH Outlet after 127,000 hours.

569°C/1056°F, 2,500 psi/17.2 MPa



(But at higher temperatures: Multiple laminations form)



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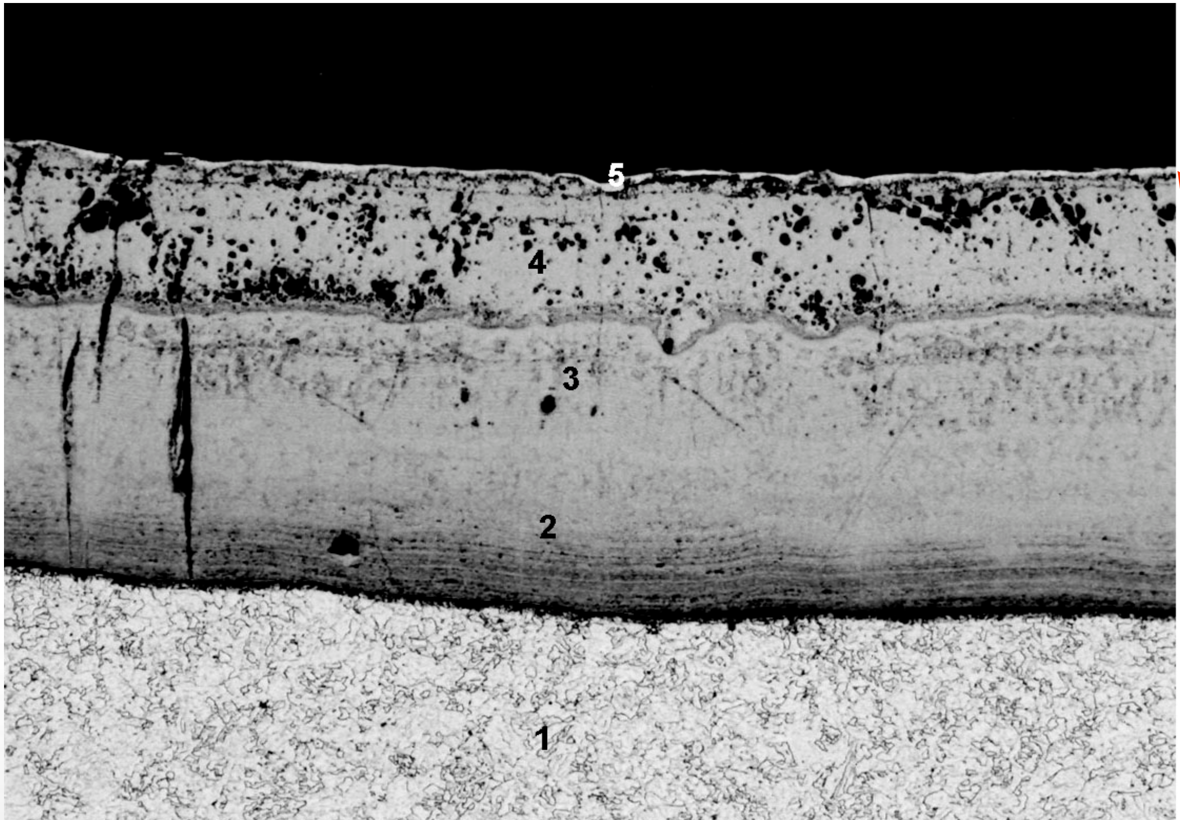
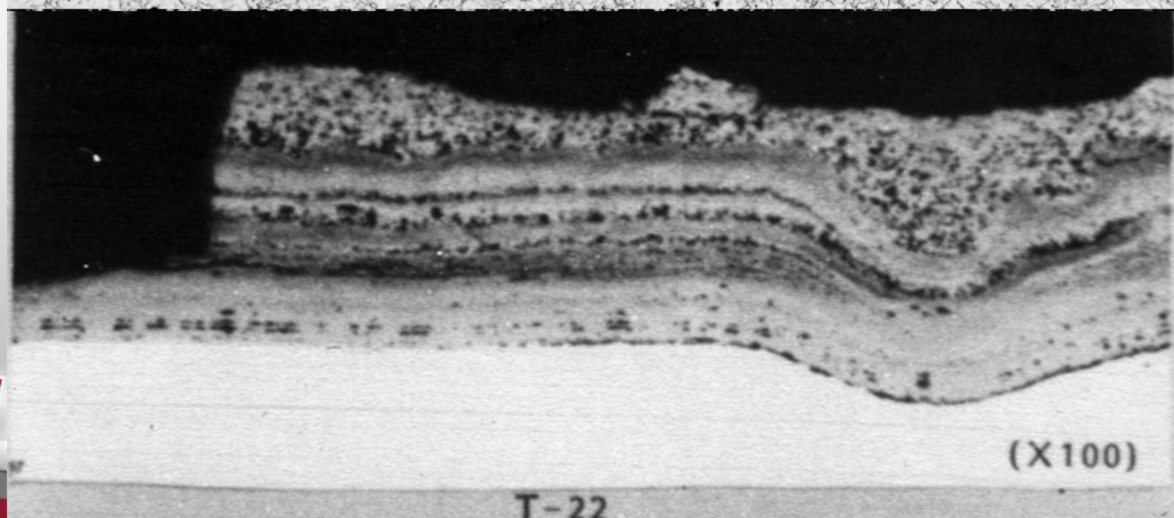
T22 in 3rd SH Outlet

OGEI 4. Multiple laminations eventually lead to exfoliation



Note Fe_2O_3

OGEI 5. Exfoliation



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Some Differences to "Established" Ferritic Picture

The oxide morphologies of the T/P23 Alloy in steam

Looks the same as T11, 12 & 22 but -----

We need to keep a careful watch on T23 tubing in HRSGs and examine as many samples as possible

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Differences to "Established" Ferritic Picture

The oxide morphologies of the T/P23 Alloy in steam

(Fe – 2.15%Cr, 1.64%W, 0.22%V, 0.22%Mn)

OGEI 5

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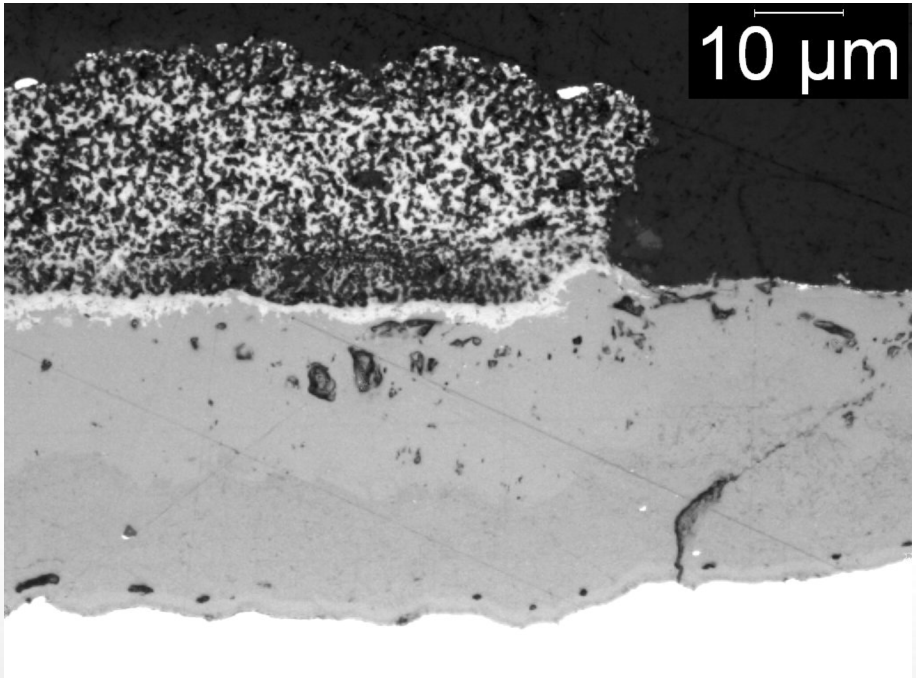
Looks the same as T11, 12 & 22 but -----

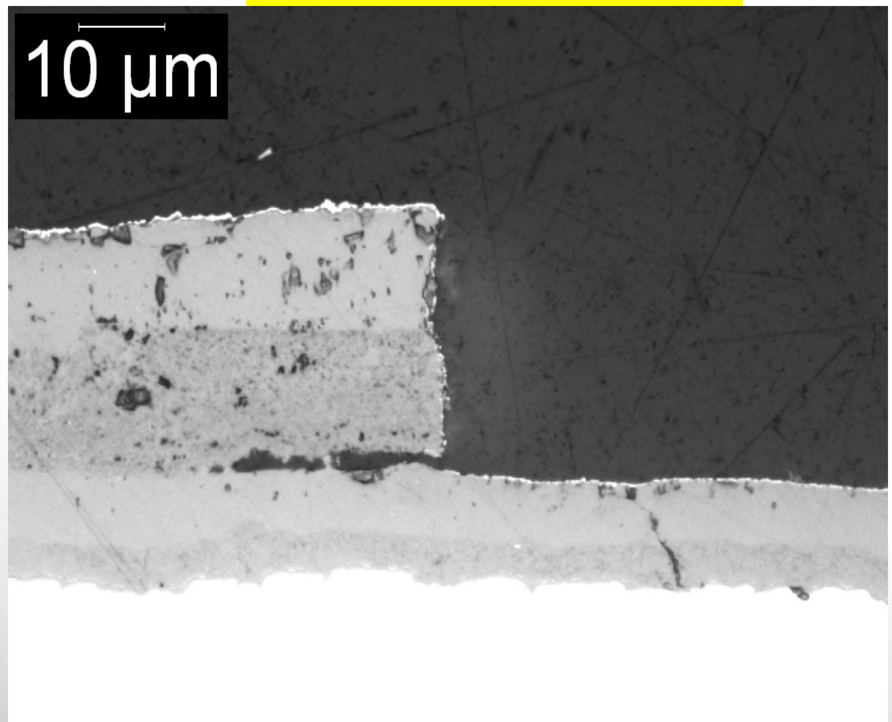
Variable Exfoliation from T23 Alloys

(Fe – 2.15%Cr, 1.64%W, 0.22%V, 0.22%Mn)



HRSG

Conventional Boiler



OGEI 5

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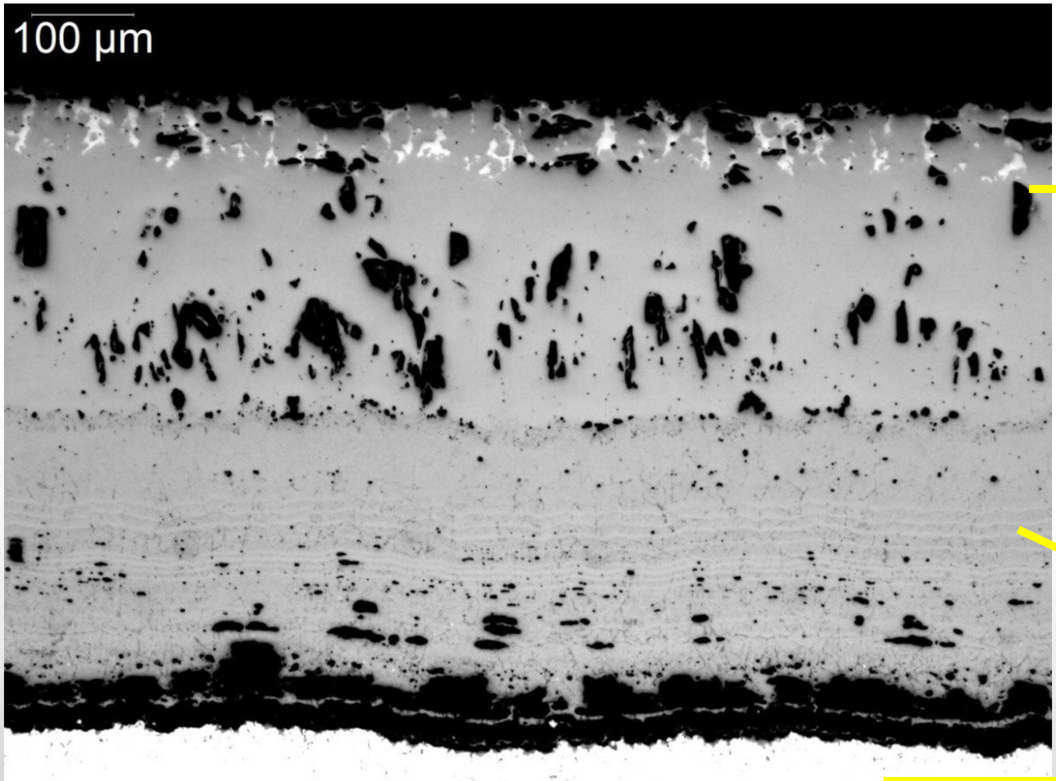
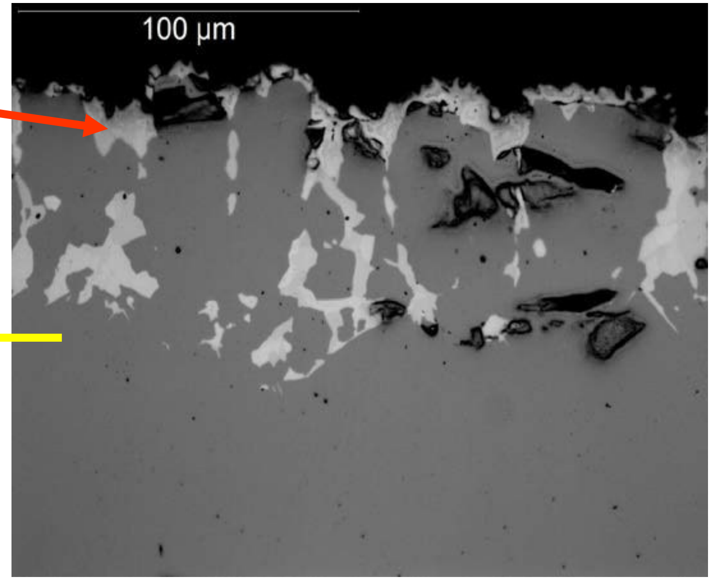
Primary Reheater T23 Tubing. 31khrs.

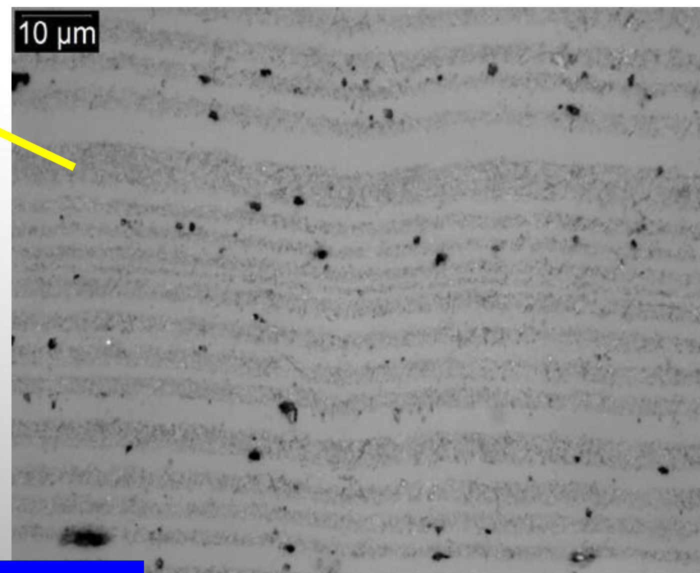
Steam 565°C (1050°F)

(Fe – 2.15%Cr, 1.64%W, 0.22%V, 0.22%Mn)

Note Fe_2O_3







OGEI 4

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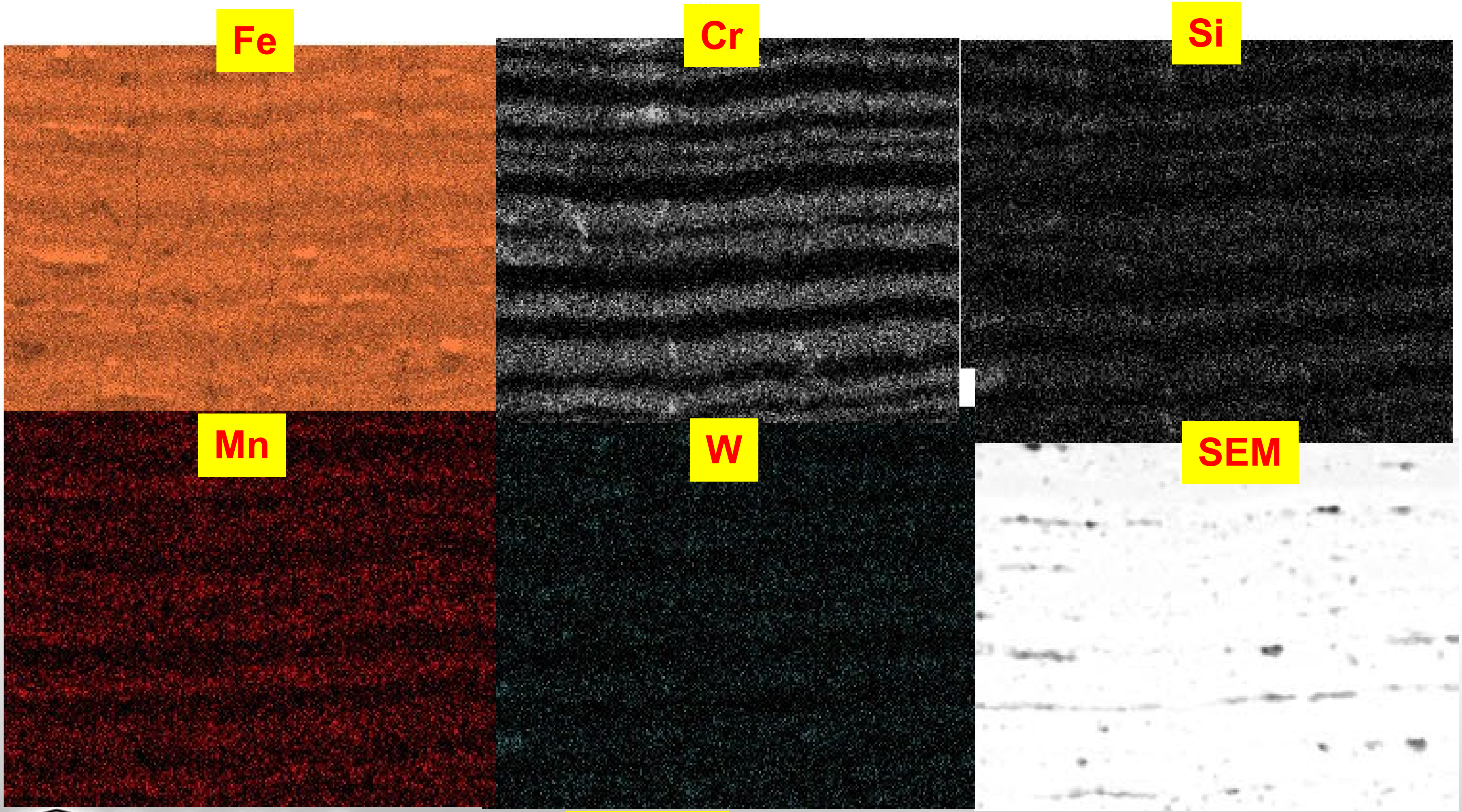
Dooley/Wright, PPChem 2019

Primary Reheater T23 Tubing. 31khrs.

Steam 565°C (1050°F)



OGEI 3

Some Differences to "Established" Ferritic Picture

The oxide morphologies of the T/P91 Alloy in steam

Looks the same as T22, T11, T12 but -----

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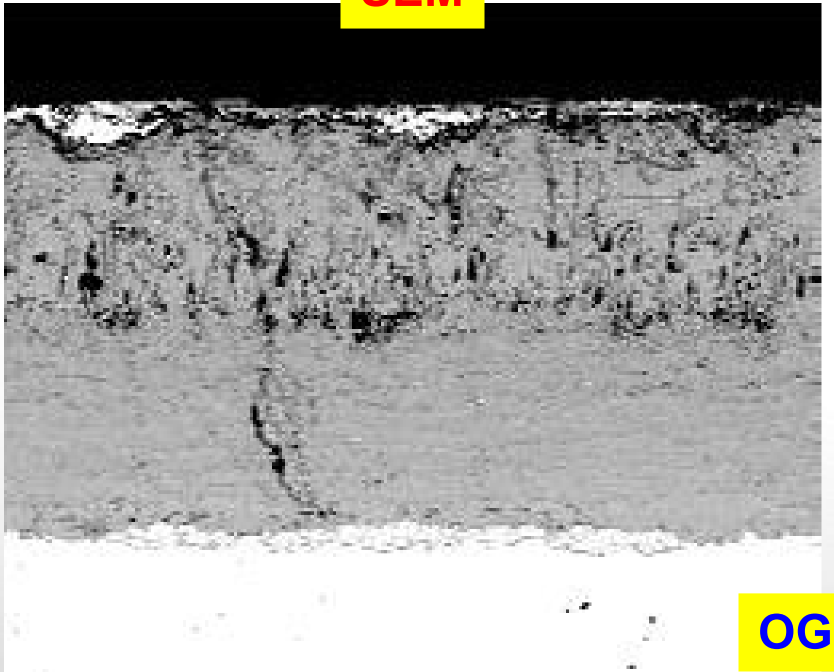
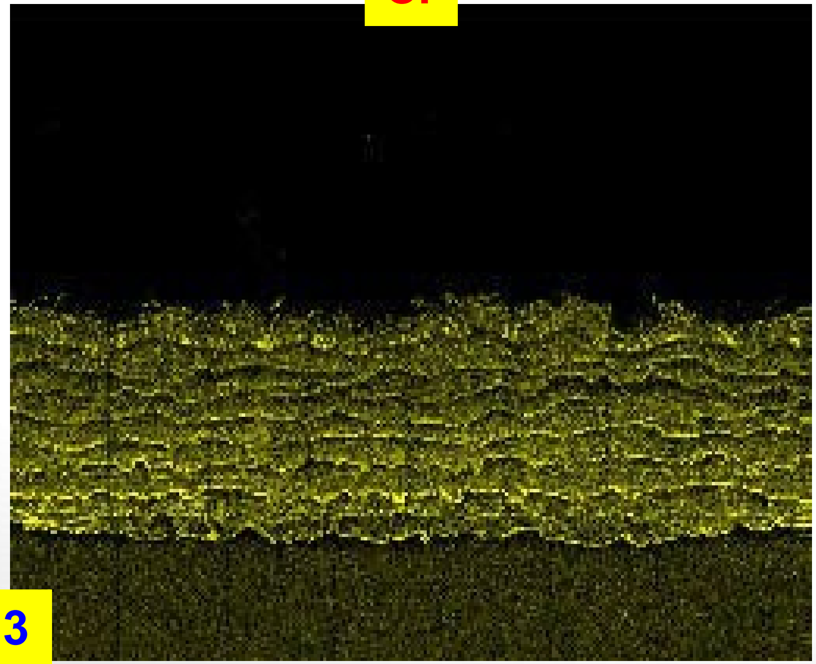
Differences to “Established” Ferritic Picture

The oxide morphologies of the T/P91 Alloy in steam

(Fe, 8.7%Cr, 0.9%Mo, 0.4%Mn, 0.23% V and Si)





OGEI 3

Looks the same as T11, 12 & 22 but the inner layer consists of chromium-rich bands within the magnetite.
Usually large regions of hematite.

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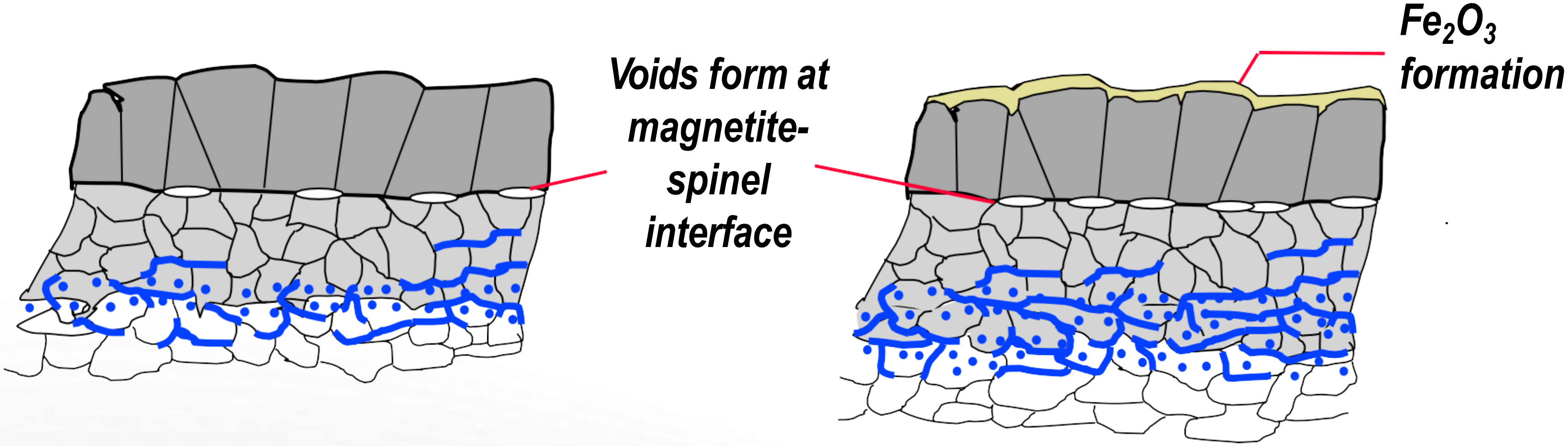
Suggested Development of Cr-rich Bands in the Internal Oxide Layer Formed on T91 Ferritic Steel



3. As oxidation rate slows, Cr-rich oxide precipitates start to form semi-continuous layers along alloy grain boundaries

4. Incorporation of the Cr-rich layers results in Cr-rich bands in the inner layer; decreasing oxidation rate allows conversion of magnetite to haematite

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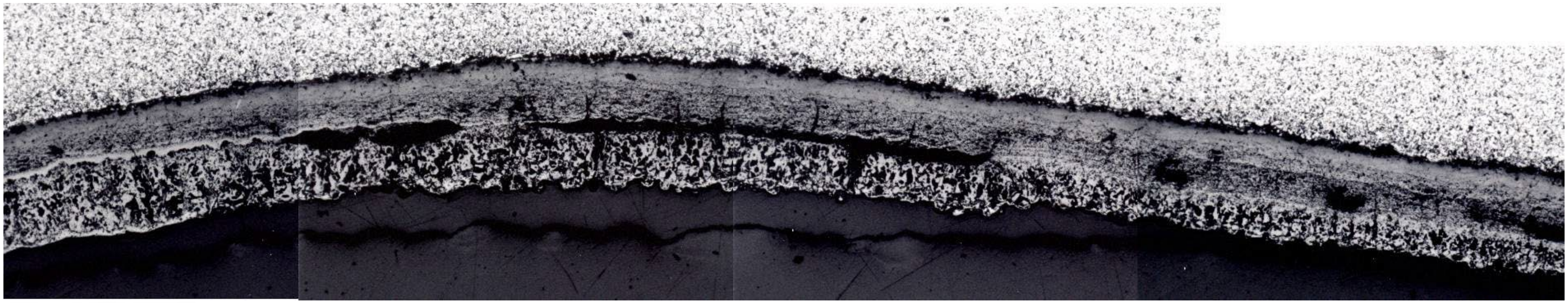
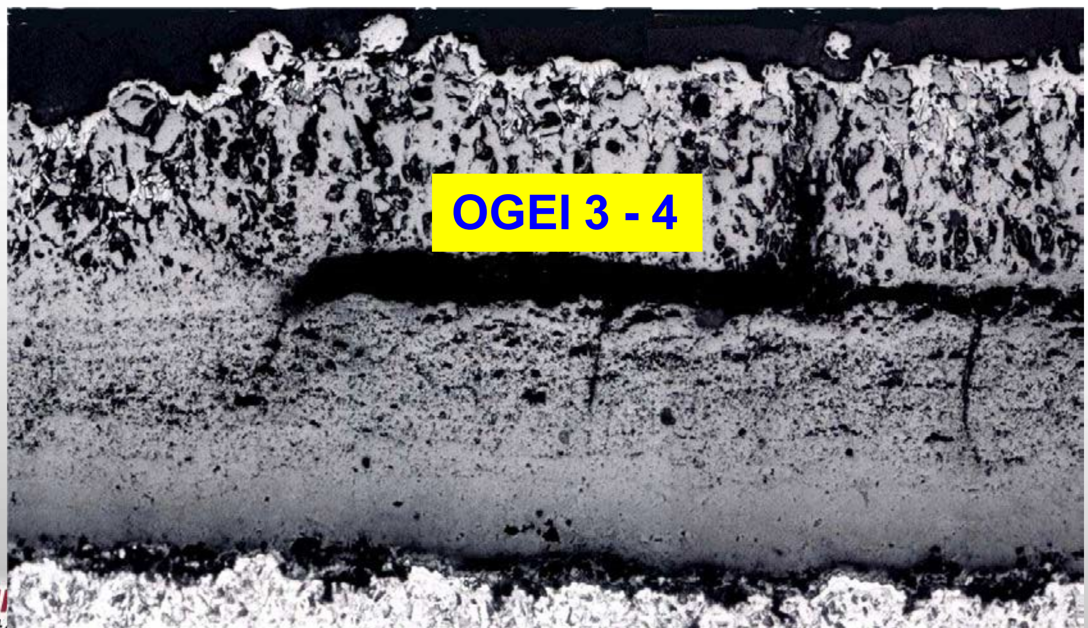
Adapted from Wright/Dooley, Materials at High Temperatures, 2011

T91 Steamside Scale Delamination

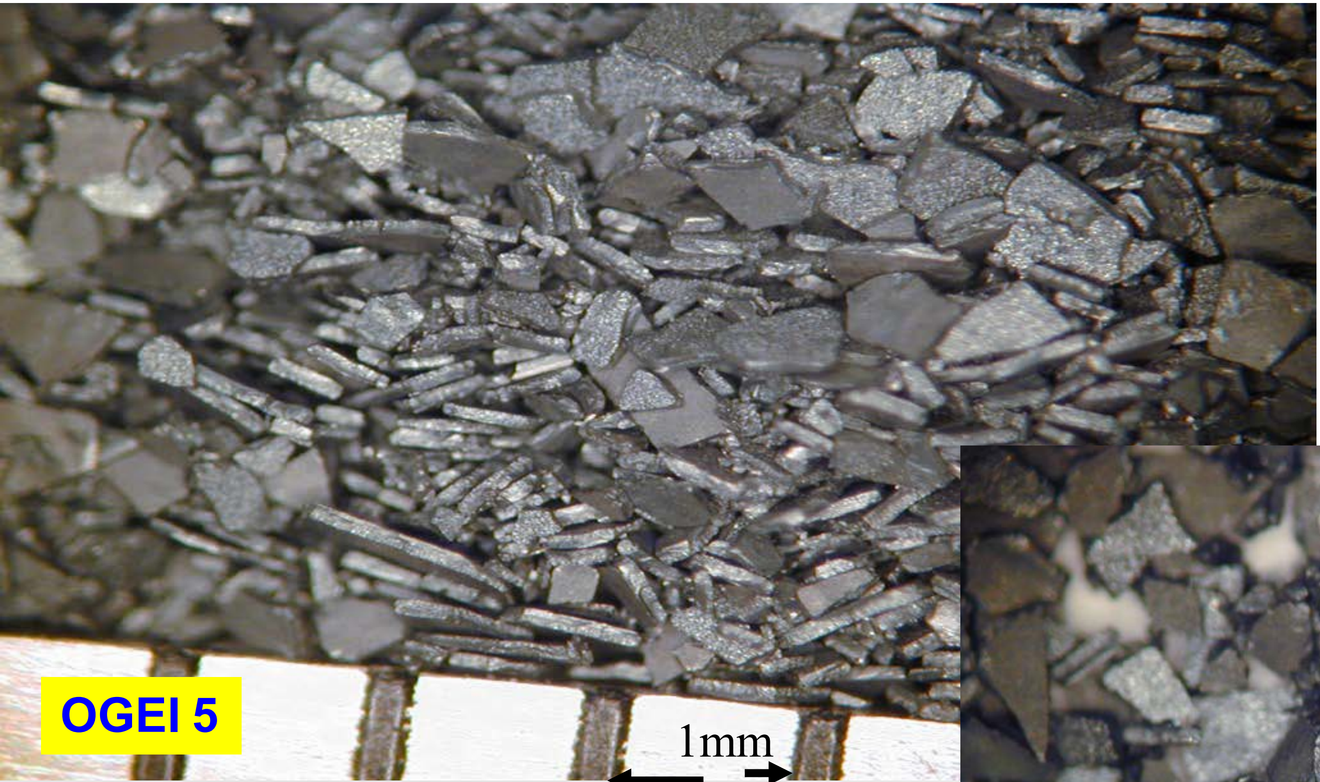
(Steam: 565°C 1050°F. 61k hrs to first LTOC Failure. Estimated temperature at failure 670°C 1250°F)

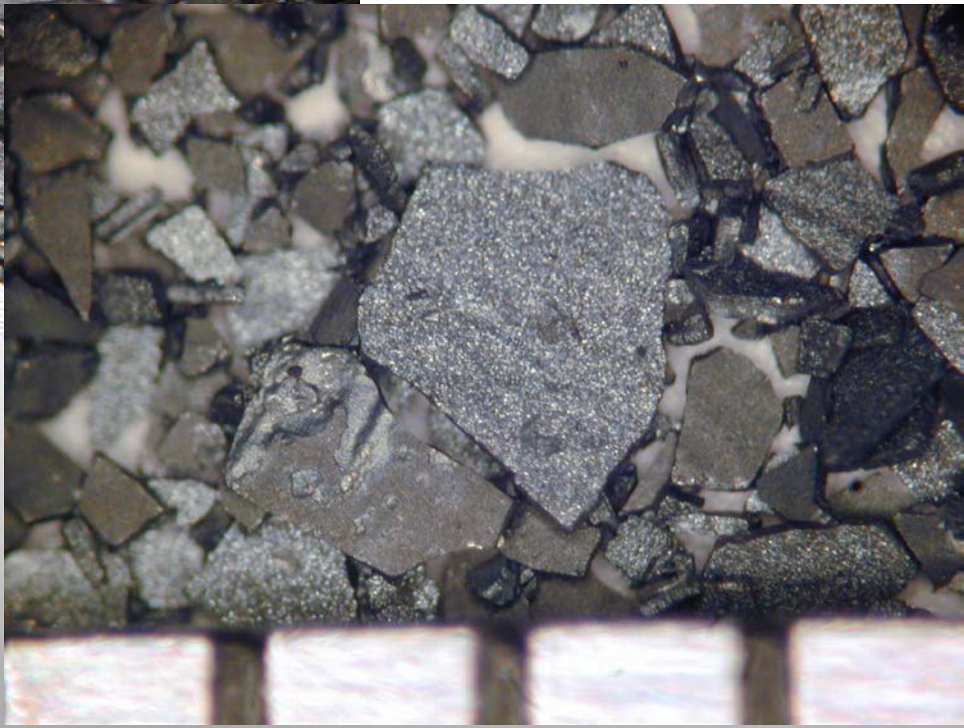




Dooley & Paterson, South Carolina, 2003

Massive Exfoliation in HRSG P91 SH Header





UK HRSG

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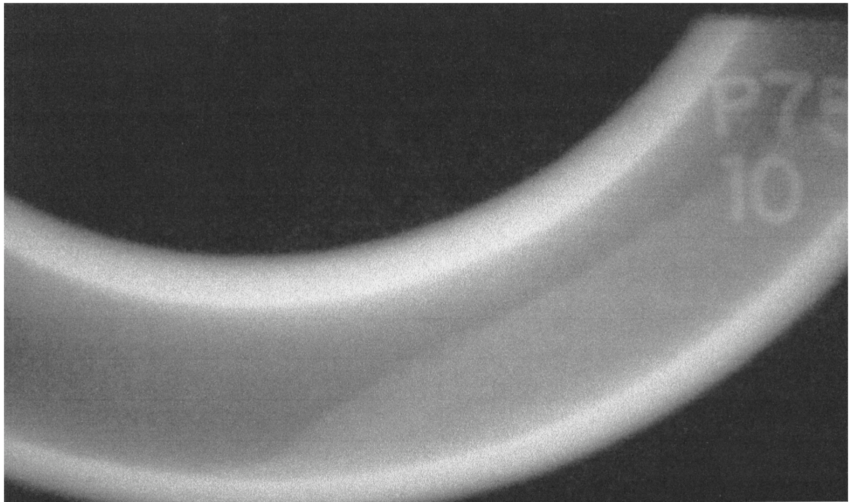
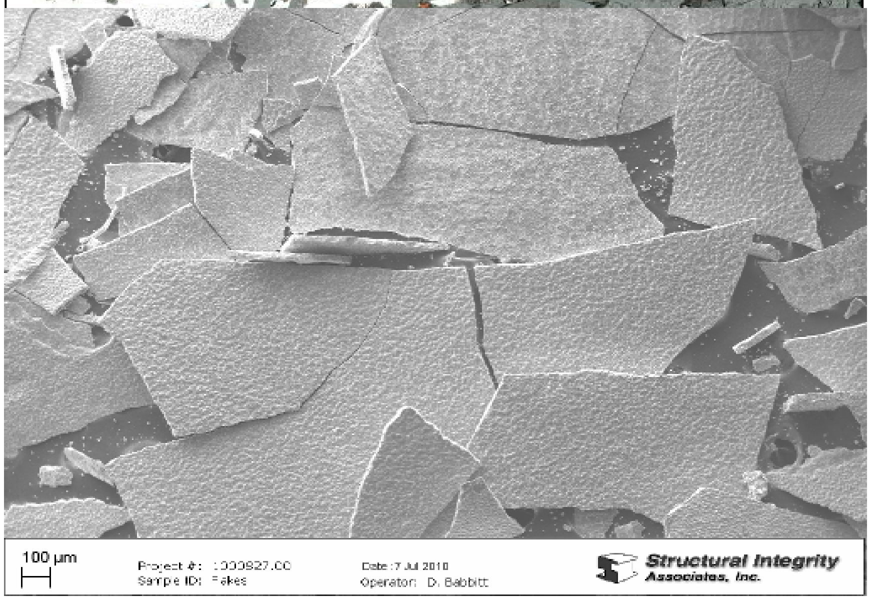


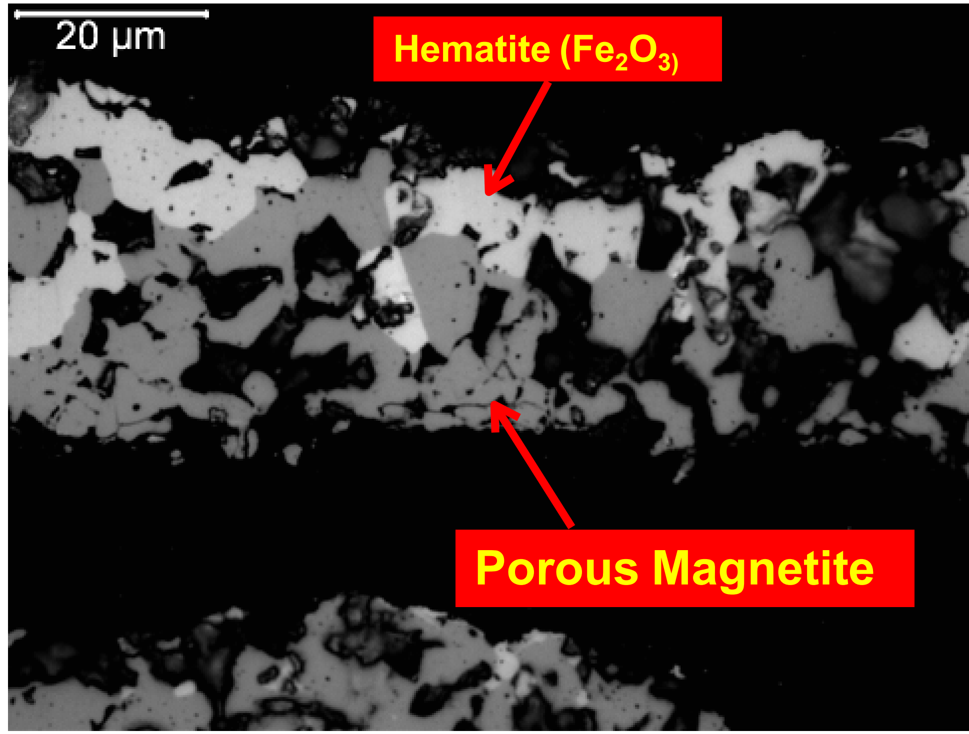
Oxide Growth and Exfoliation (OGE) on Austenitic Materials in Steam

In fossil plants OGE sometimes results in Short-term overheating due to blockages at SH bends

Austenitic alloys are rare in HRSGs

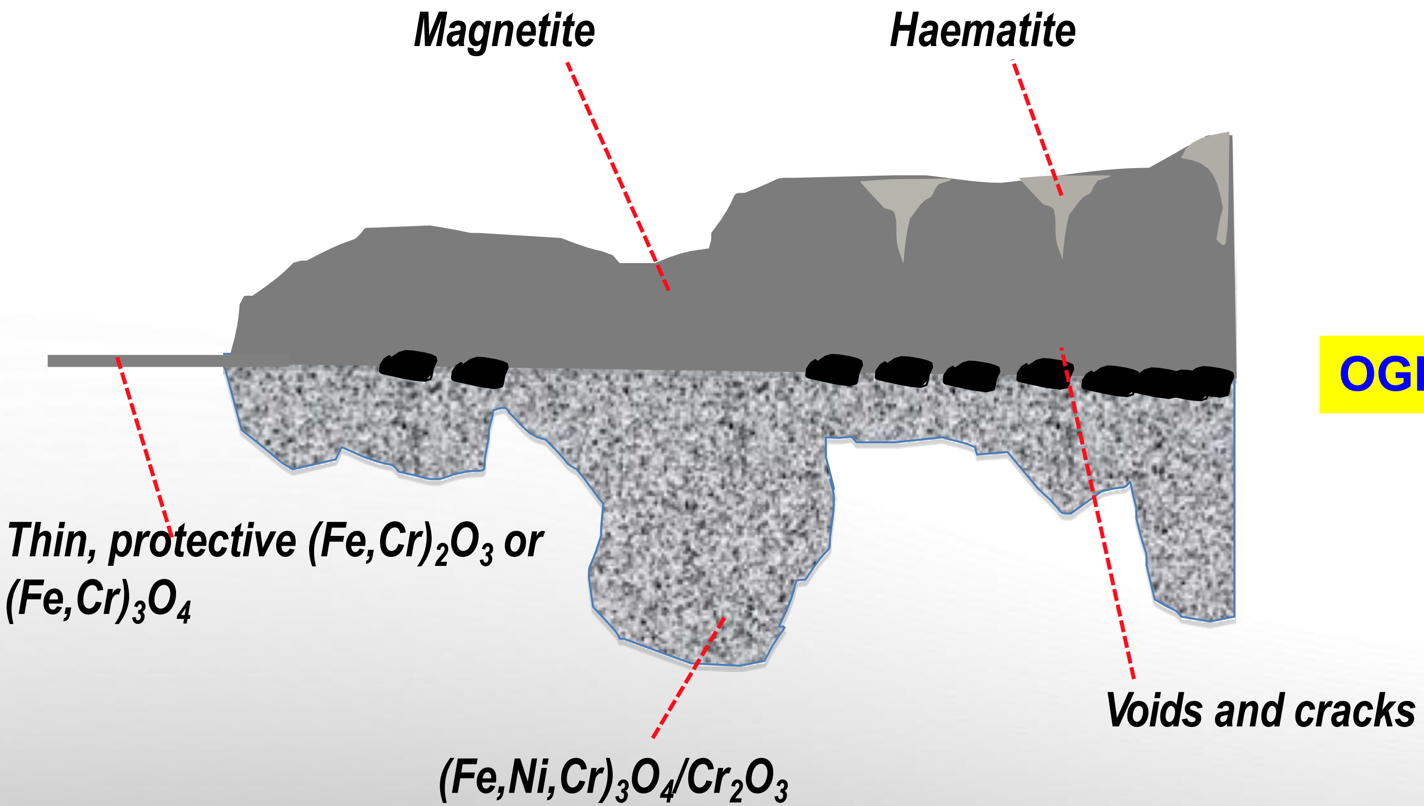
Exfoliated Oxide from 347H in SH after 7 Months





USA 2011

Schematic for an actual steam-grown oxide scale on an Austenitic Alloy



OGEI B

Wright/Dooley, Materials at High Temperatures, 2011

Morphological Index for Oxide Growth and Exfoliation (OGEI) on Austenitics (304, 321, 347, H alloys, HFG Alloys and Internally Treated (Shot peened))

A. Initial duplex oxide with an outer magnetite and inner spinel. Initially there is no hematite in outer part of magnetite until voids form at Oxide/Oxide

B. Initiation of voids between the duplex layers. Voidage accumulation at base of magnetite. Hematite starts to form on outside surface of the magnetite. There is never any laminations in the inner layer.

C. Growth of voids along the O/O interface into continuous voidage and then to cracking

Examples included on next few slides

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Sources: ABHUG and EHF 2017. Dooley/Wright, PPChem 2019

Morphological Index for Oxide Growth and Exfoliation (OGEI) on Austenitics (304, 321, 347, H alloys, HFG Alloys and Internally Treated (Shot peened))

D. Exfoliation. Only of the outer magnetite (plus some hematite) once the density of voids/cracks and hematite along the O/O interface reaches a critical percentage

E. Following exfoliation there is regrowth of magnetite on the spinel and this follows the morphological development in A.

Examples included on next few slides

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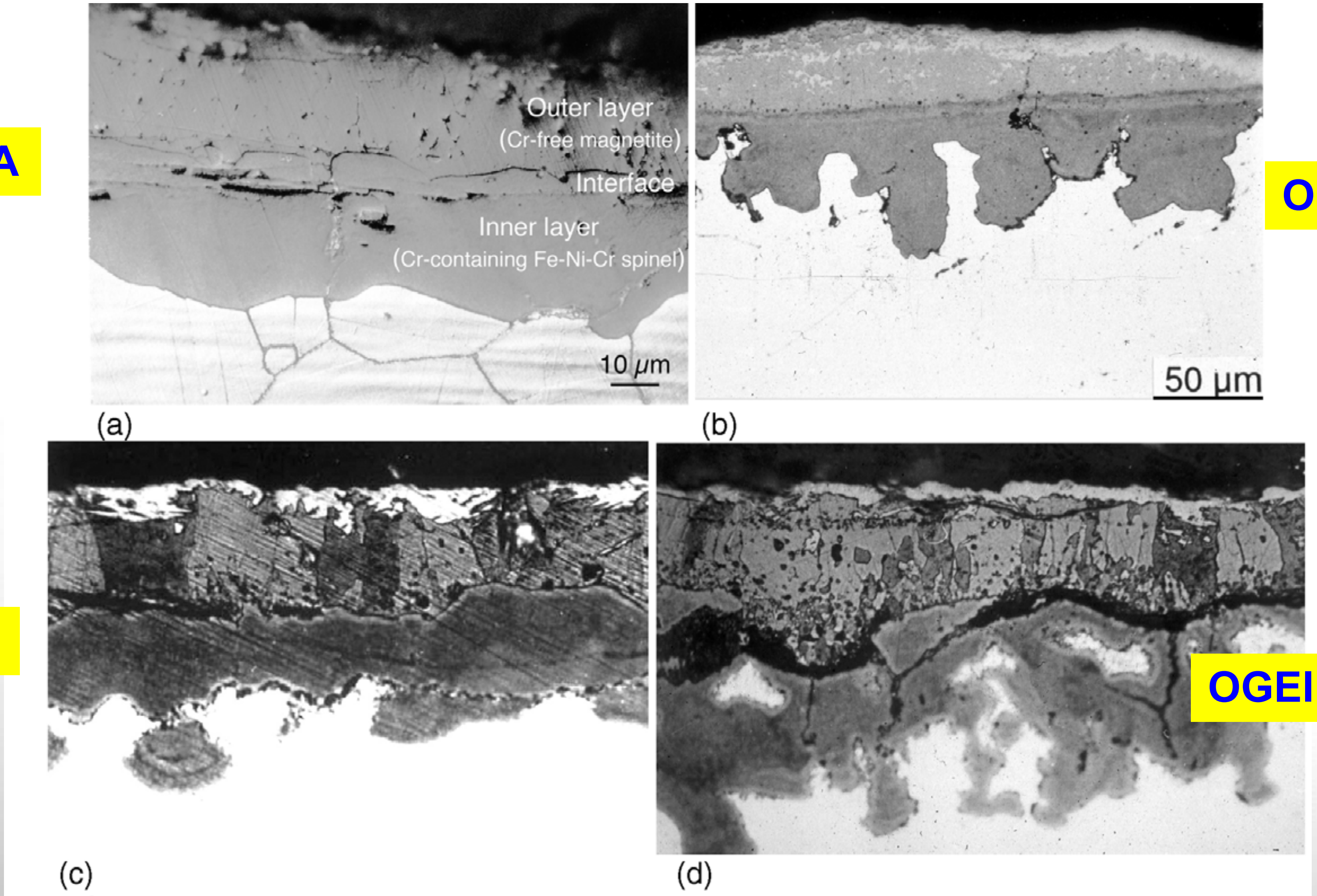
Sources: ABHUG and EHF 2017. Dooley/Wright, PPChem 2019

Oxide Growth and Exfoliation Sequence on "Normal" Austenitics

OGEI A

OGEI B



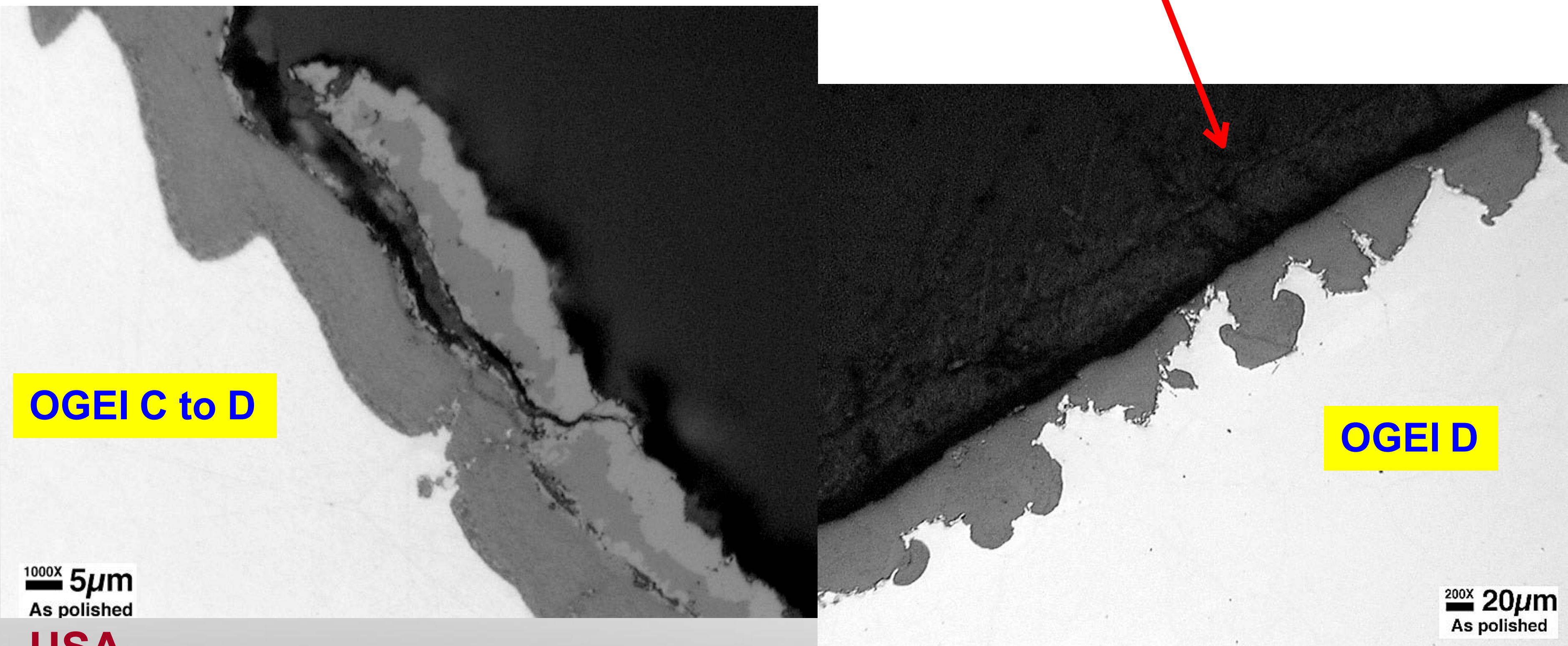
OGEI C

OGEI C to D

Canada/USA 1990s

TP 304H in SH Outlet Steam at 538°C (1000°F)

Ready to Exfoliate (1,400 hrs) and Exfoliated (26,000 hrs)



USA

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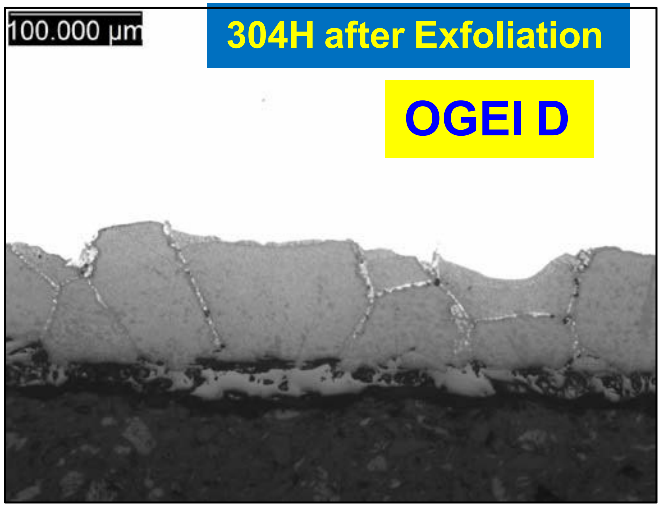
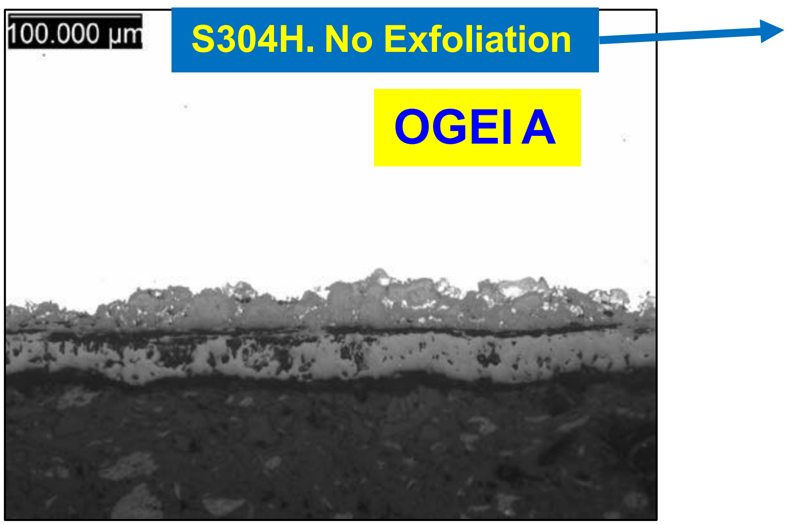
Wright/Dooley, Materials at High Temperatures, 2011

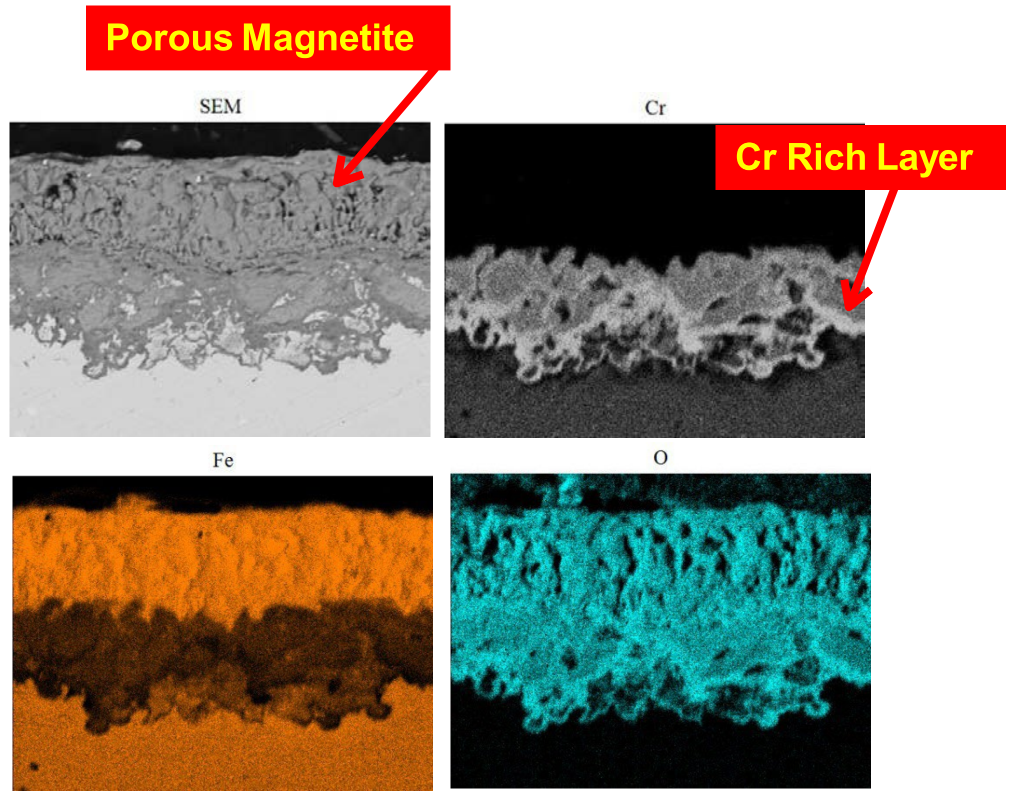
Some Differences to “Established” Picture

Oxide Morphologies Differences between 304H and S304 (shot peened)

304H and S304H in SH after 6 Months







Influences of Cycle Chemistry including FFS on OGE

and

Using the OGE Data Base to identify Deposits and the Origin of the Oxides

Steam grown oxides are semiconductors and grow by counter flux ionic diffusion processes of Fe^{2+} moving outwards and O^{2-} (oxide ion) moving inwards. Superheated steam with temperatures up to 600C +
Mechanism is covered in Dooley/Wright papers

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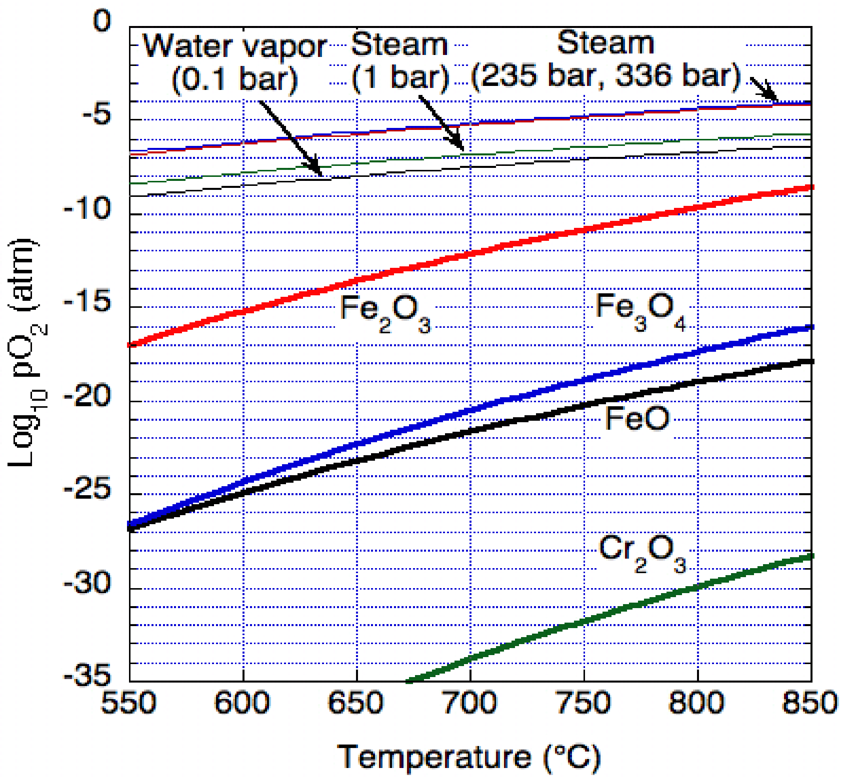
Growth and exfoliation of oxides in steam do not depend on the steam chemistry (oxygen levels)

but on the partial pressure of oxygen: $k = \log[(pO_2)_{eq_{y/2}}] = -\Delta G_o/(2.303RT)$

and pO_2 in steam is sufficient to form all oxides of Fe, Cr…



1. Levels of oxygen in steam have no effect on the OGE processes

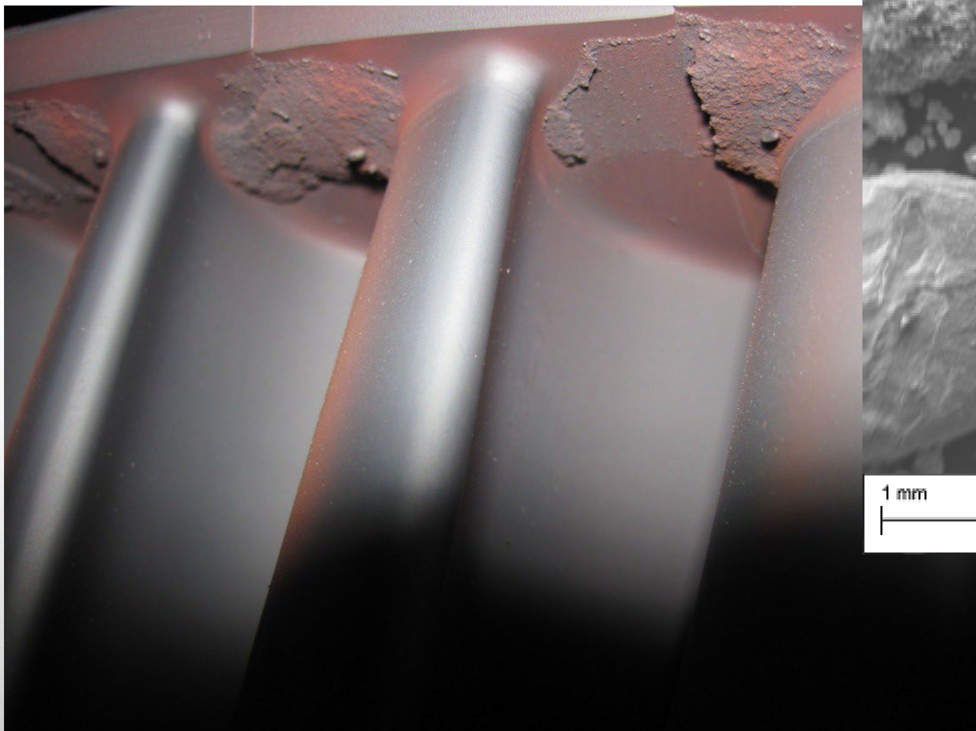
2. Major discussion worldwide. How an FFS film will form on these surfaces. Possibly only during shutdown condensation phases. Can film exist at steam temps up to 600°C and what is mechanism for changing rate or morphology, if any?

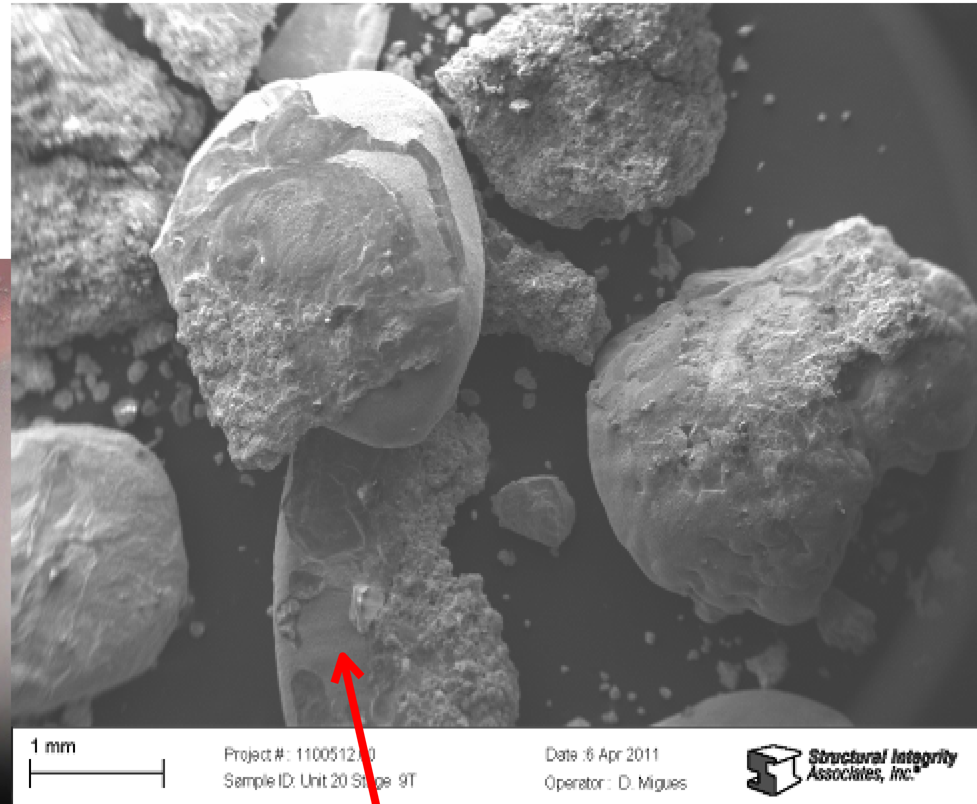
3. Formation of FFS Film on surface is expected to: a) change the dissociation constant of steam? b) only have an effect when condensate is present?

Source: Wright/Dooley, Materials at High Temperatures, 2011

Example: Use of OGE Information: Steam Turbine Deposits

Reheater materials: T23, T/P 91

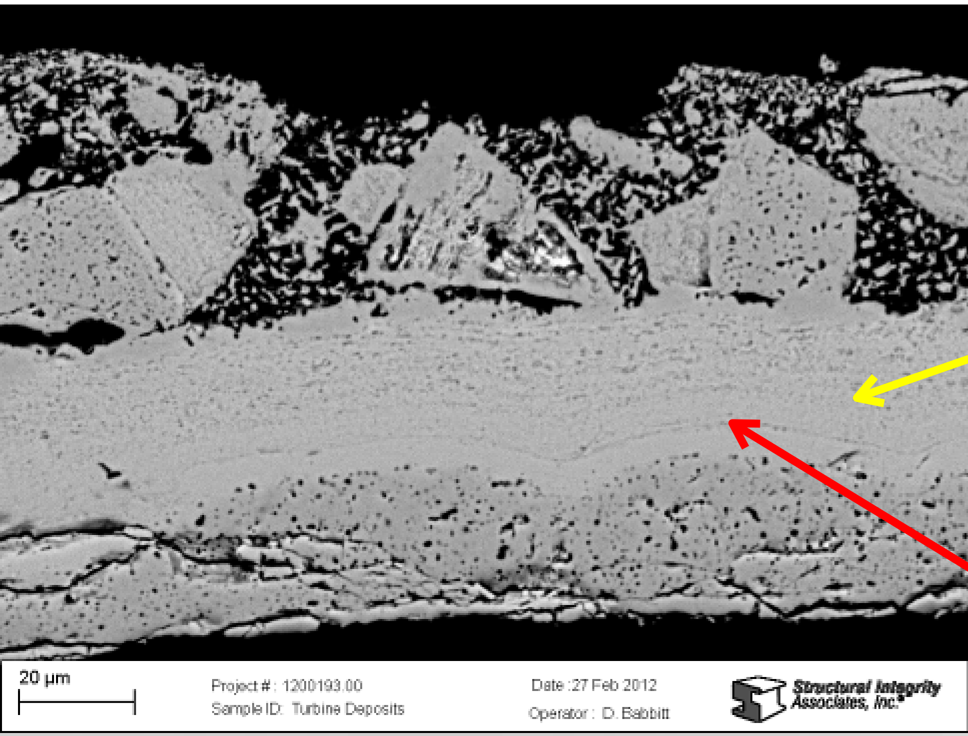


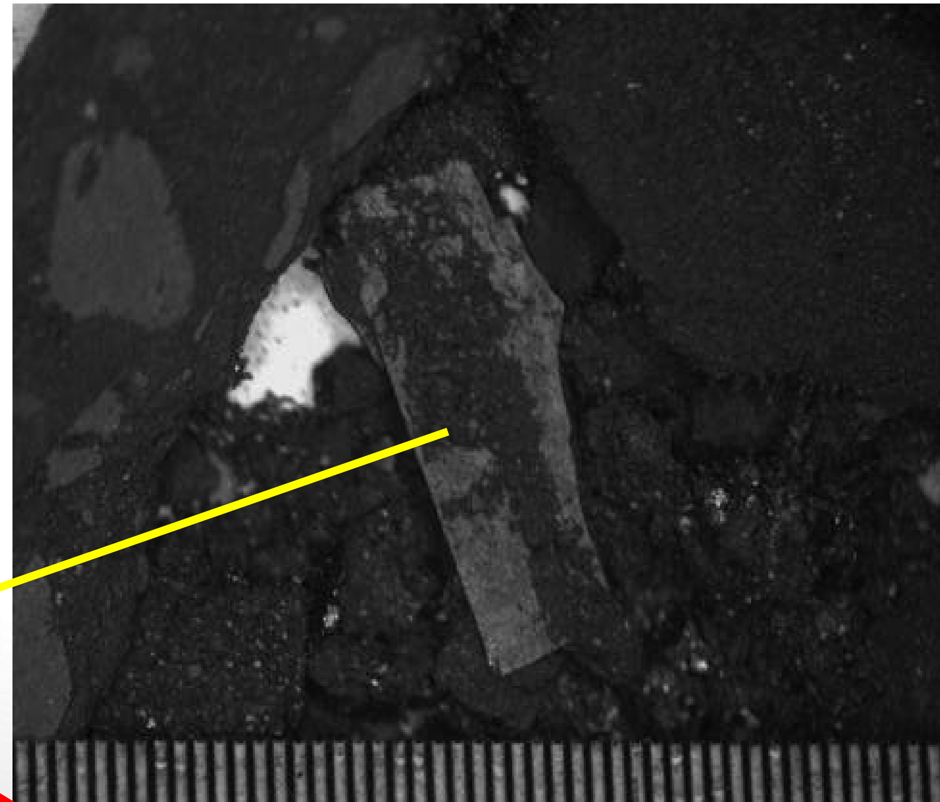


5.5 % Cr
0.9 % Mo

Example: Use of OGE Information: Steam Turbine Deposits

Triple - pressure HRSG with ACC and with reheater materials: T 23, T/P 91



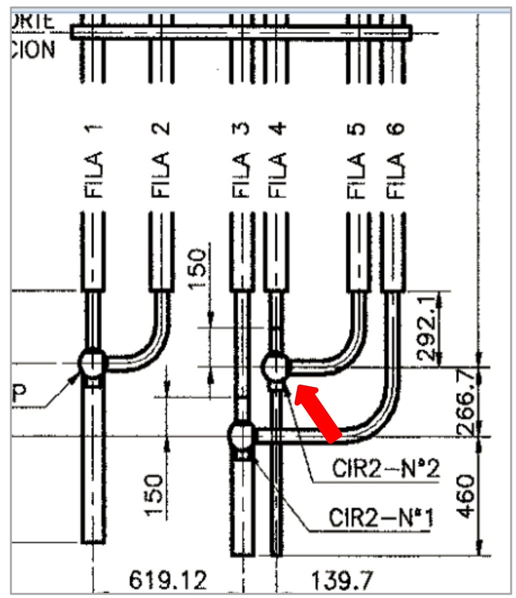


2.3 % Cr
1.4 % Mo

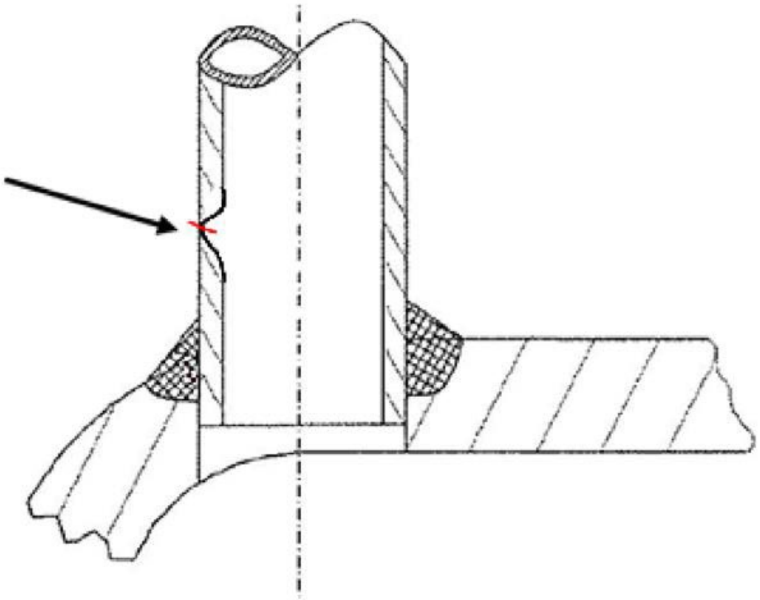
RH Tube Failures
Example of Oxide Growth and Exfoliation (OGE)

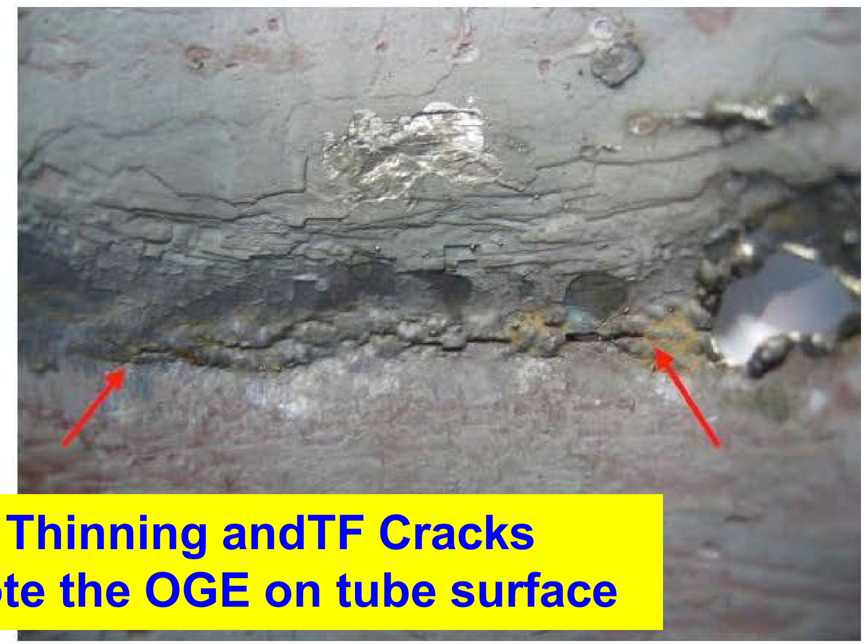
Originally presented by Barry Dooley, Bob Anderson & Sergio Gomez, BBE, Spain. EHF2019, Greece

Note:
Discoloration of failed tube and end of header. Wide gap between modules



RH2 TUBE LEAKS (T/P22)

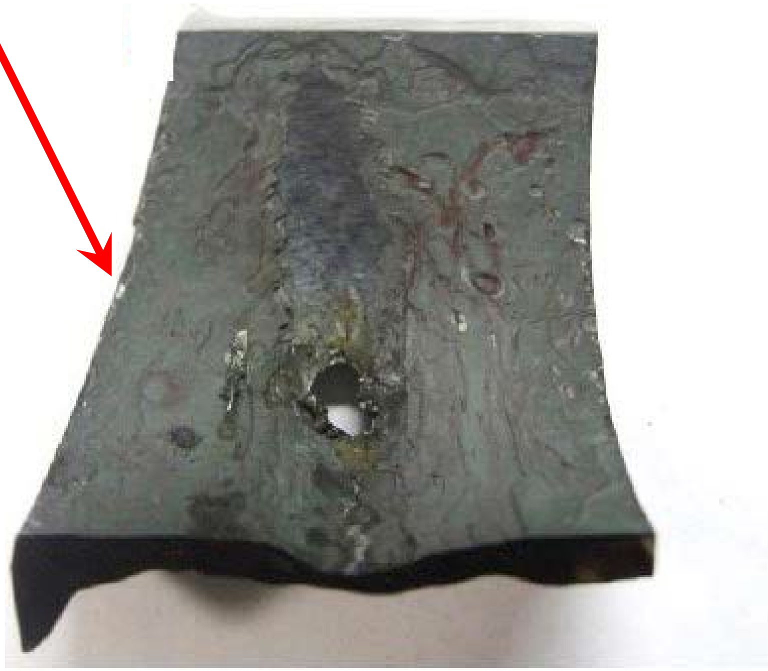




Circumferential Wall Thinning andTF Cracks
Between Arrows Also note the OGE on tube surface

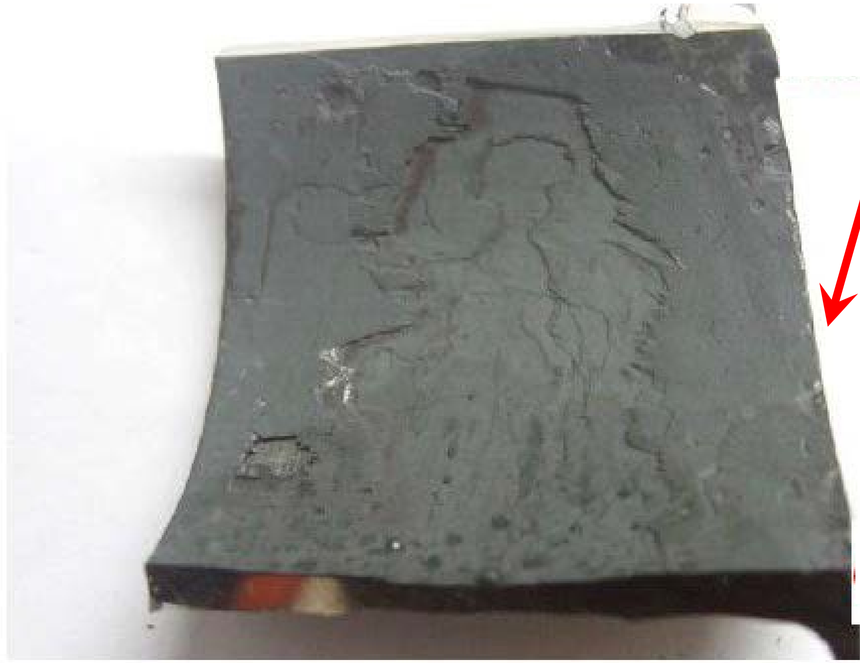
Interior Surface of RH Tube

Weld @ Header



Bottom of Tube

Weld @ Header



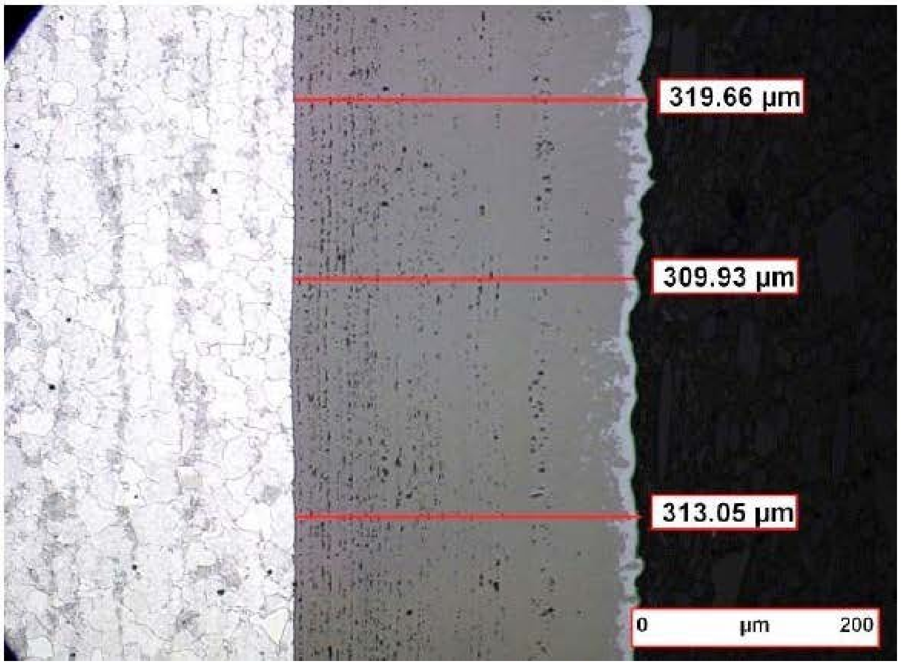
Top of Tube

Note: Quite severe exfoliation

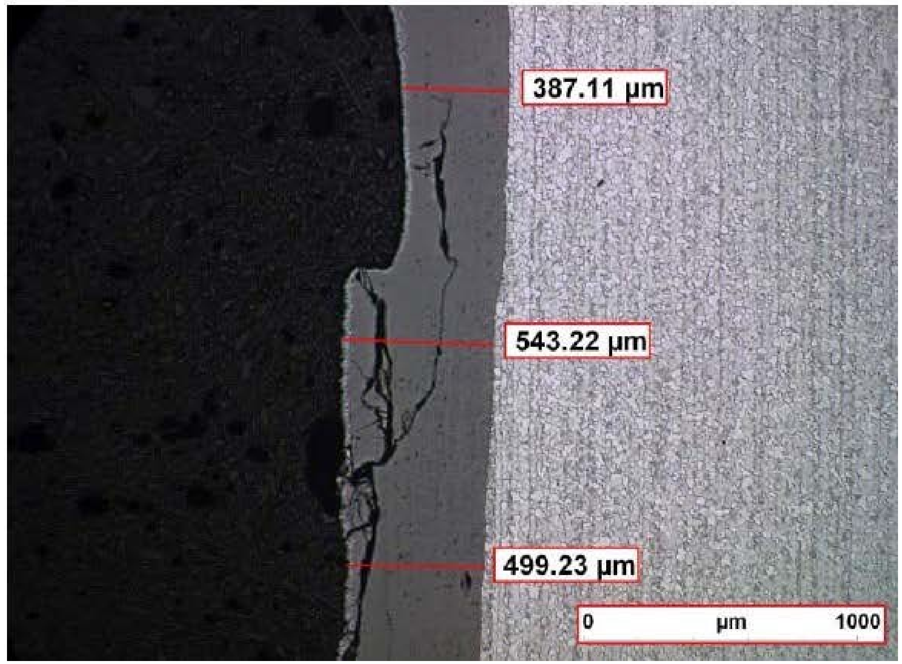
Micrograph – Circumferential Section

Away From Failure Zone

Note here that oxide is OGEI 3

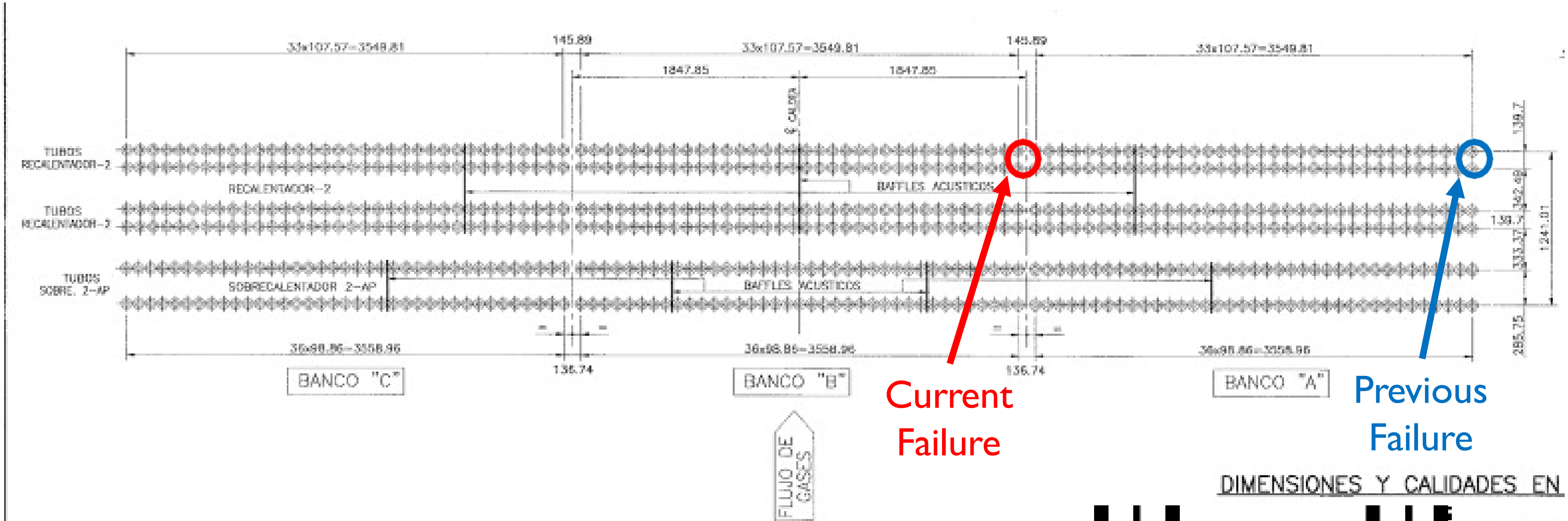


Note here that oxide is OGEI 4 and shows exfoliation

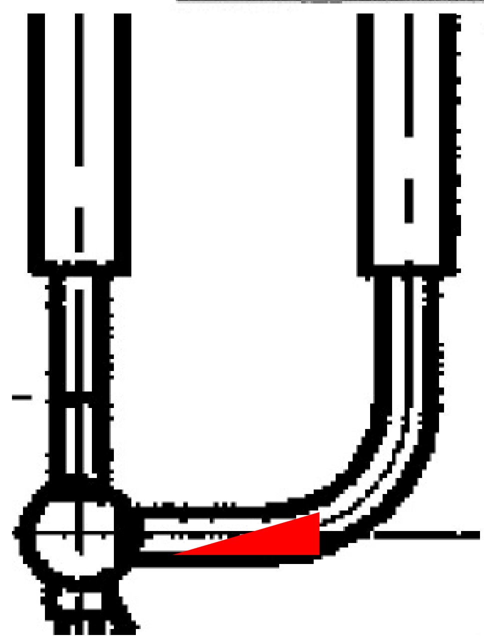


Oxides Much Thicker Than Near Failure Zone

Mechanism and Root Cause of RH2 Failures



- Similar RH leak 11 months previous in sister at sidewall gap
- Thick oxide spalls at high strain locations
- Repeated spalling (OGE) thins tube wall
- Oxide spalled from portion of vertical tube partially or fully blocking horizontal section?
- Increasing metal temperature & oxide growth rate (materials degradation observed)



In Summary

On Oxide Growth and Exfoliation (OGE) in Steam and Relation to some common problems

- There is an established morphological picture and indices for OGE on “normal” ferritic & austenitic alloys and for T23, T91 and fine grain and shot-peened austenitics
- There is NO effect of cycle chemistry on OGE, There is currently uncertainty on any influence of FFS
- The time & operating regime of exfoliation are known
- The oxides on T11 and 22 can lead to SPE
- The oxides on austenitics can lead to STO
- The oxides on T91 can result in LTOC or STO
- The oxides from T91 and T23 can lead to ST deposits and maybe performance loss

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Acknowledgements

- John Stringer: Who introduced the intricacies and importance of oxide morphologies at the University of Liverpool and for 25 years at EPRI
- Jim Westwood at Ontario Hydro. One of the original compilation of OGE was developed for the Canadian Electrical Association (CEA) in 1983
- Steve Paterson (Aptech/Intertek): We embellished the original compilation into publications, compilations and strain areas, 1987-2003
- Ian Wright: Who became interested during his EPRI sabbatical, then in the Oxide Group at ORNL (now “Retired” but co-author of the three OGE papers referenced)
- Wendy Weiss: Who has conducted the OGE metallography over the last 10 years at SI
- 100s of utilities/operators worldwide who have unfortunately shared their failures and damages

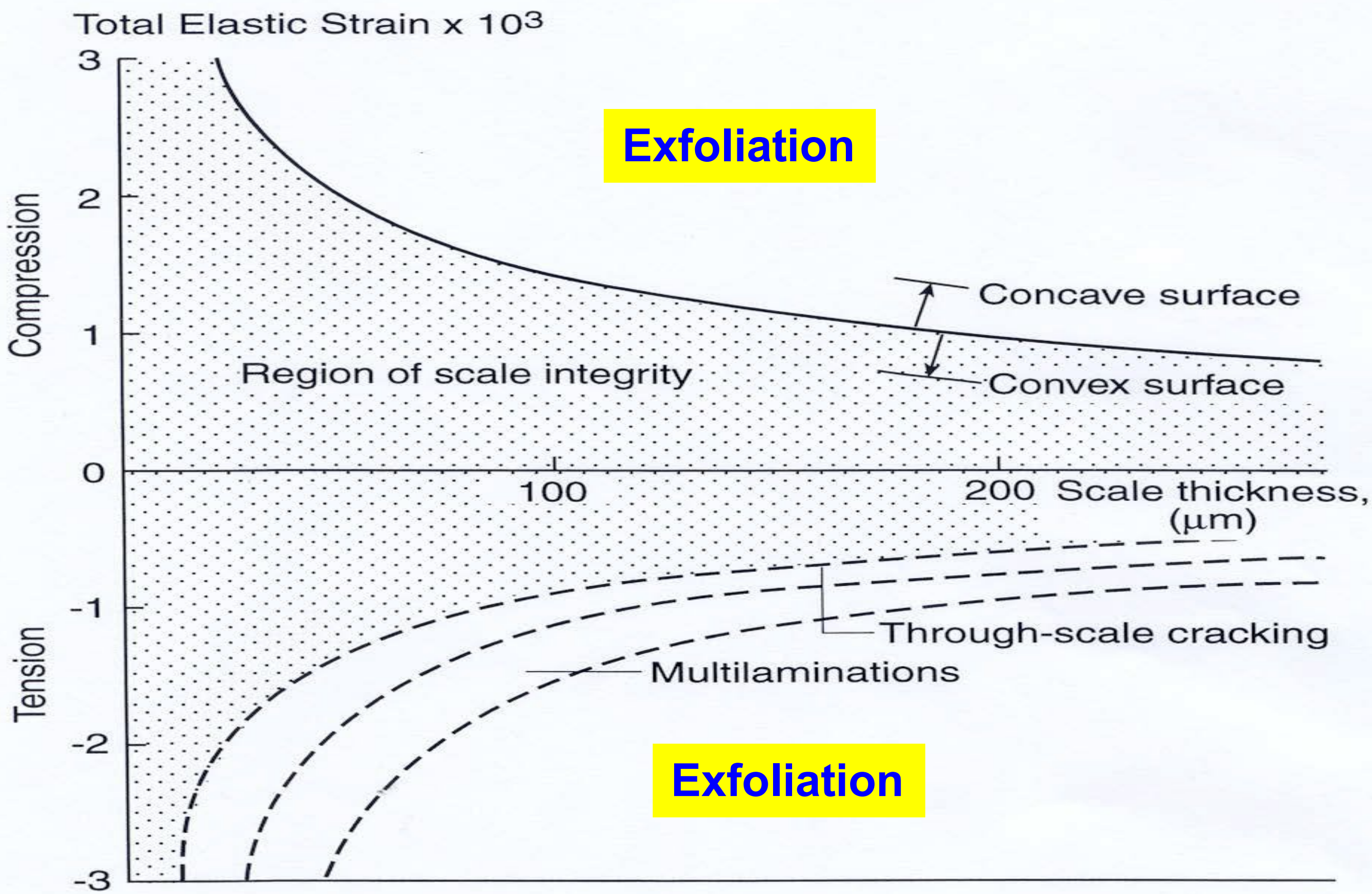
A few additional slides

Most Common Questions Worldwide
On Oxide Growth and Exfoliation (OGE) in Steam

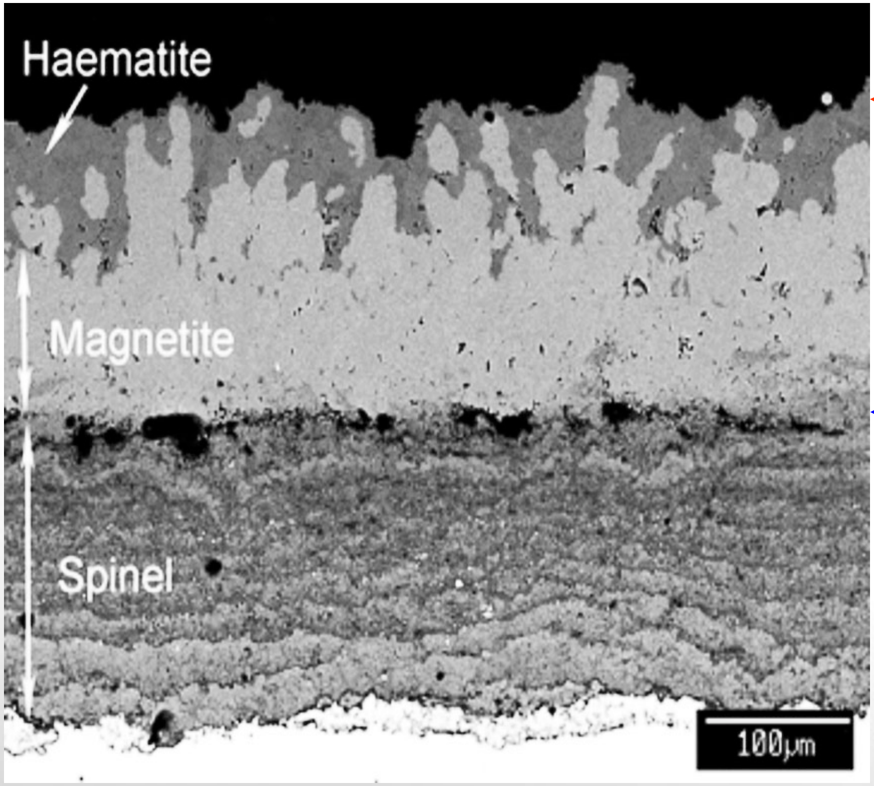
- Why are some oxides laminated and some not?
- Which materials/oxides cause longterm and short-term overheating?
- Which materials/oxides are responsible for solid particle erosion of steam turbines
- What isthe effect of the cycle chemistry on OGE?
- Should we use T91 or Austenitics in our new plant
- Can we operate T91 above 600°C/ 1112°F
- How does T23 perform in steam?

Oxide Failure Map

Developed Originally by Armitt et al 1978



T91 Tubing. 64kh at 1051°F/566°C



Note Fe_2O_3

Note Voids

OGEI 3

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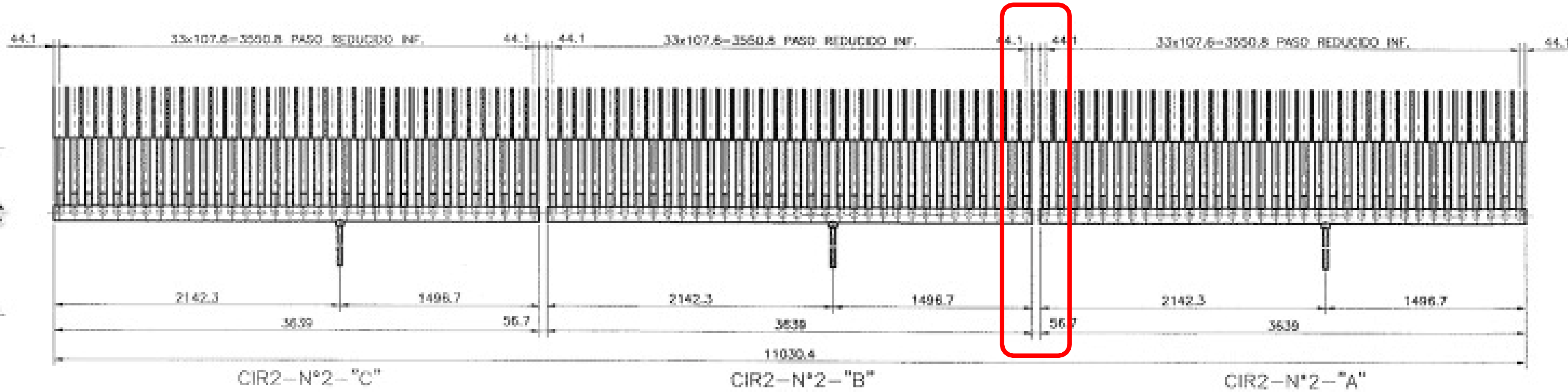
Dooley/Wright, PPChem 2019

Oxidation Limits for SH / RH Tube Materials

T11	550°C
T22	580°C
T23	580 - 600°C
T91	600 - 610°C
300-series Austenitic	700°C

Extracted from Dooley/Wright, PPChem 2019

Hypothesis



- No gas baffles in gaps between modules
- Higher gas velocity in gaps = higher tube metal temperature
- Higher tube temperature = thicker internal oxide and higher OGEI
- Thicker oxide = higher tube metal temperature
- 25 µm of oxide increase tube wall by ~2°C