The Changing Face of Corrosion In Coal-Fired Boilers

J. F. Henry, J. V. Nava

ALSTOM

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The Problem

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Increasingly Restrictive Emissions Requirements Governing Equipment Operation Have Led To Significant Changes In The Environment To Which Materials Are Exposed.

Example: Low NOx Firing Systems In Coal-fired Utility Boilers (Outlet Steam Temperatures >950°F)

Enormous Potential Impact On Equipment Reliability

The Problem

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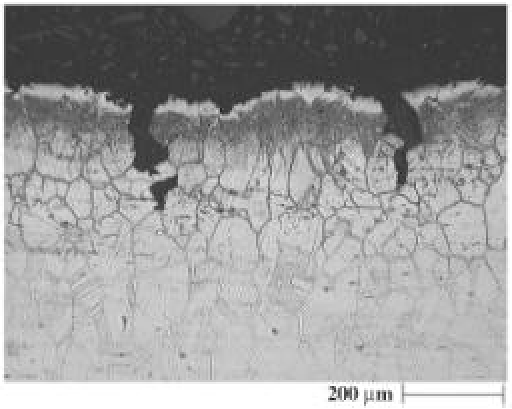
An Example Of The Changes Encountered:

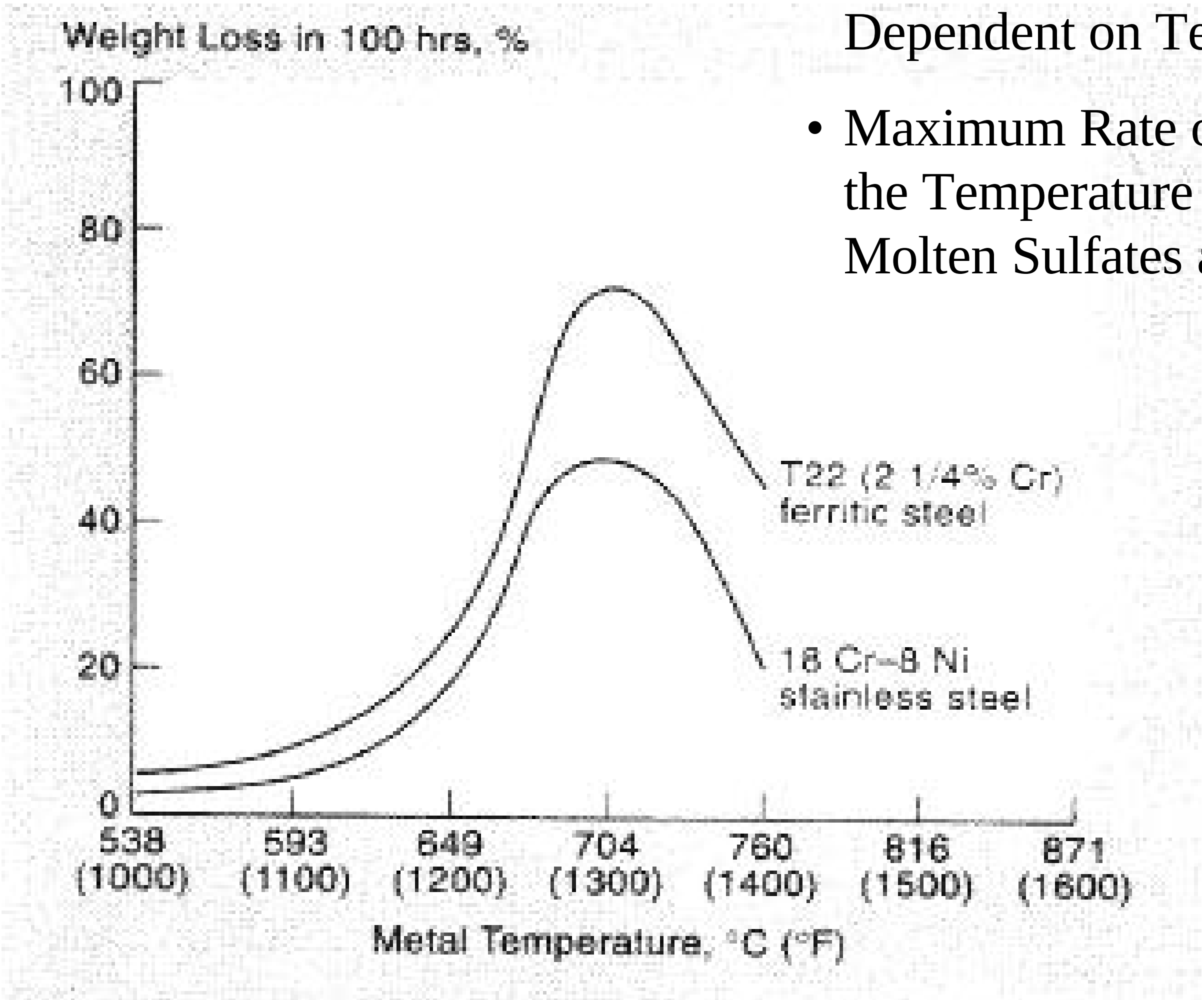
Coal-Ash Corrosion In High Temperature Steam-Cooled Tubing (Superheater & Reheater)

“Traditional” Explanation For Coal-Ash Corrosion



- **Presence of Molten Iron-Alkali Sulfates**
- **Fluxing Away of Protective Oxide Film**
- **Direct Reaction Between Bare Metal and Reduced Sulfur Species**

Effect of Metal Temperature On Coal-Ash Corrosion



- Wastage Rate is Critically Dependent on Temperature.
- Maximum Rate of Attack is in the Temperature Range Where Molten Sulfates are Soluble.

According to EPRI's Boiler Tube Failures: Theory and Practice

Traditional Mitigation Strategy

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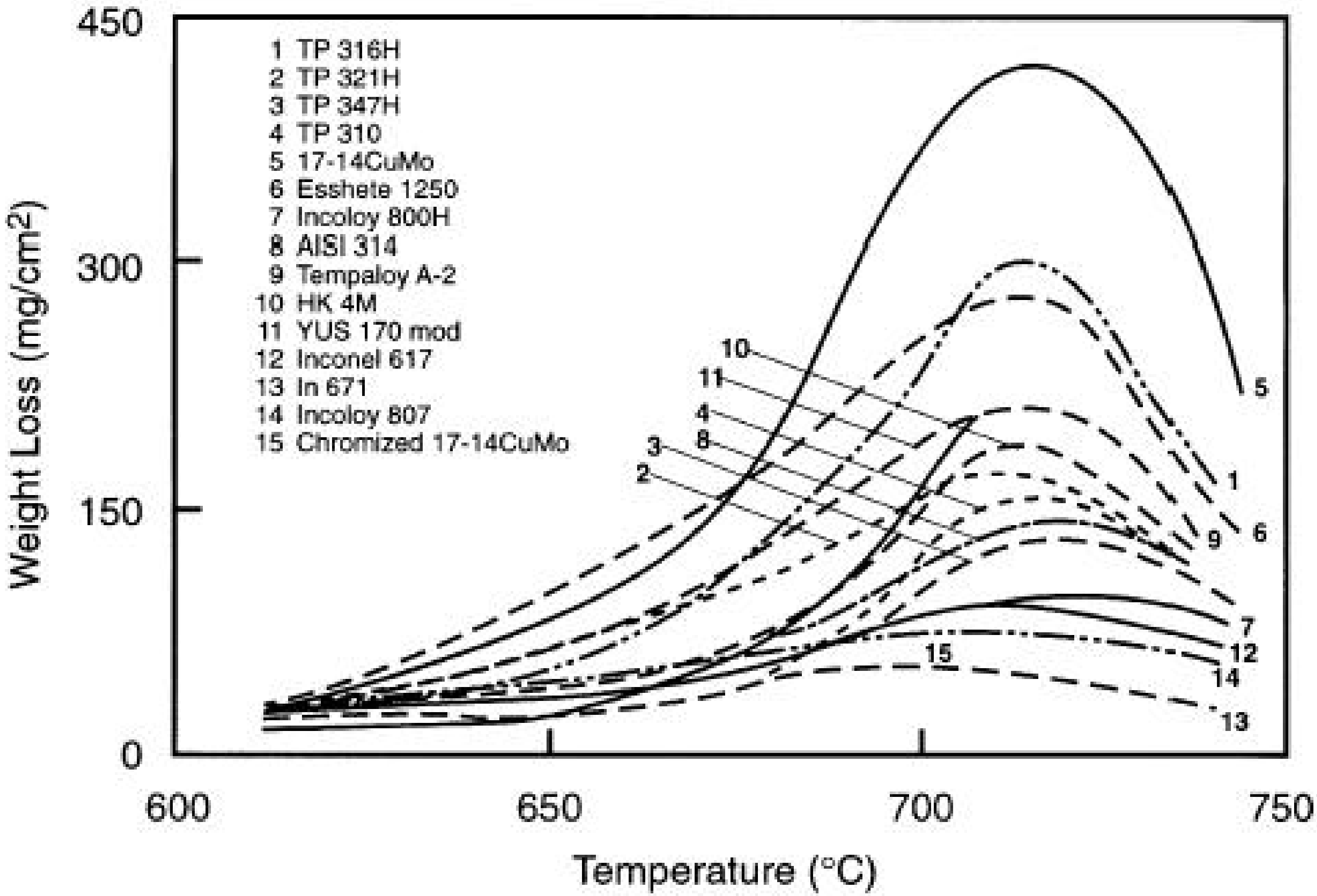
Based on Accepted Understanding of the Cause of Coal-Ash Corrosion, There Were Two Potential Options to Mitigate Effects of Coal-Ash Corrosion.

- **Option 1---lower steam temperature**
- **Option 2---install a material with better resistance – i.e., higher chromium, silicon, or aluminum content**

Traditional Mitigation Strategy – Option 1

- **Lower Steam Temperature to a Level Where Molten Phase Could Not Form**
- **Successful Experience at Eddystone Unit 1 Led to Adoption of this Strategy for the Entire US Power Industry**
- **A Primary Reason for Limitations in Overall Efficiency of Generating Cycles**

Influence of Temperature on Rate of Attack for High Alloy Materials



According to EPRI's Boiler Materials For USC Plant

Traditional Mitigation Strategy – Option 2

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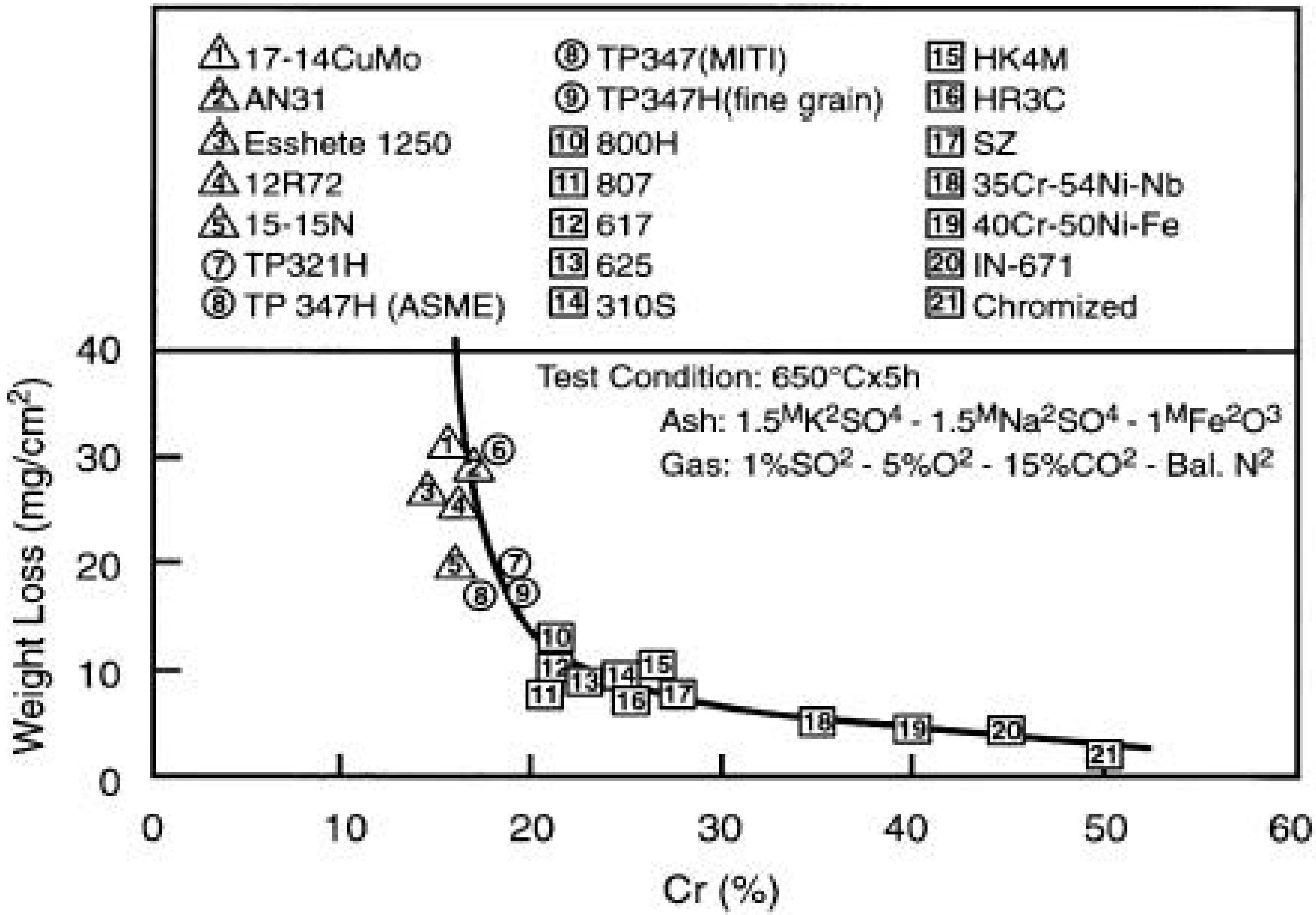
- Install a material with sufficient amount of oxide stabilizer, such as Cr, Si or Al, to resist dissolution of oxide film.
- It was demonstrated that, at temperatures between 600-650 °C, >25%Cr, 4-14% Si or >4% Al were adequate to achieve this effect.

Influence of Chromium in Combating "Traditional" Coal-Ash Corrosion



Note saturation of Cr effect above 30%

According to EPRI's Boiler Materials For USC Plant

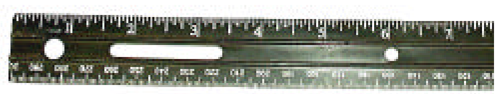
"Surprise Attack"

- **Following Implementation of Modified Firing Systems to Control NOx Emissions, Numerous Tube Failures Occurred That Do Not Fit "Classic" Coal-Ash Attack Model.**
- **Rapid Attack of HR3C RH Tubing (TP310CbN With 25%Cr) in Supercritical Boilers With 1005 °F Outlet Steam Temperature**
- **Attack Rate Exceeded 30 mpy, Virtually Identical to that of TP304H (18% Cr).**

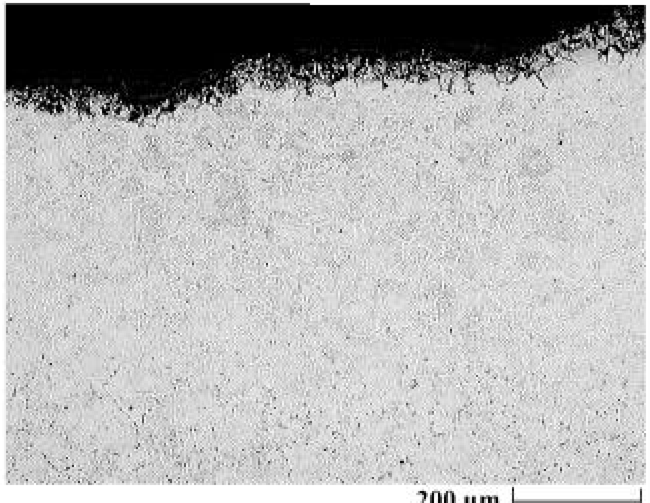
Carburization Effect

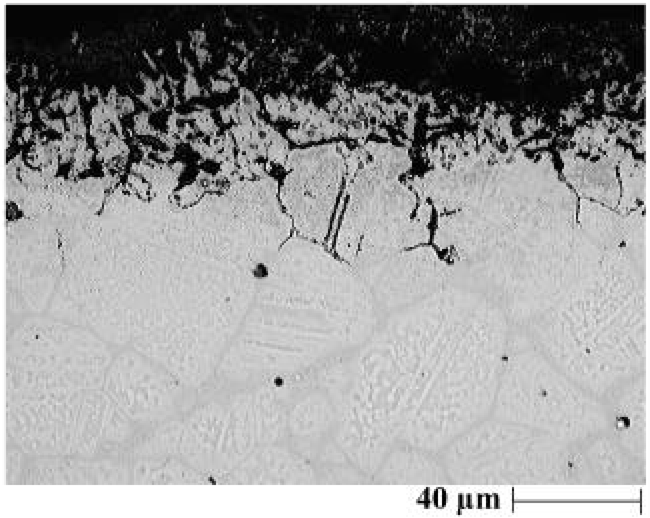
- A Common Feature of the Ash Accumulated on the Tube Surface
  - High Level of Carbon
  - Source of Carbon--Unburned Coal Particles Due to Inadequate Combustion (Low Levels of Oxygen)
  - Highly Reducing “Micro-Climate”
- Effect of Localized High Carbon Potential
  - Diffusion of Carbon Into Tube Surface
  - Reaction With Cr to Form Carbides, Thereby Reducing Cr in the Matrix That Stabilizes Protective Oxide Film
  - Molten Phase Does Not Appear to be Necessary

Example of Modified Coal-Ash Corrosion Of Stainless Steels

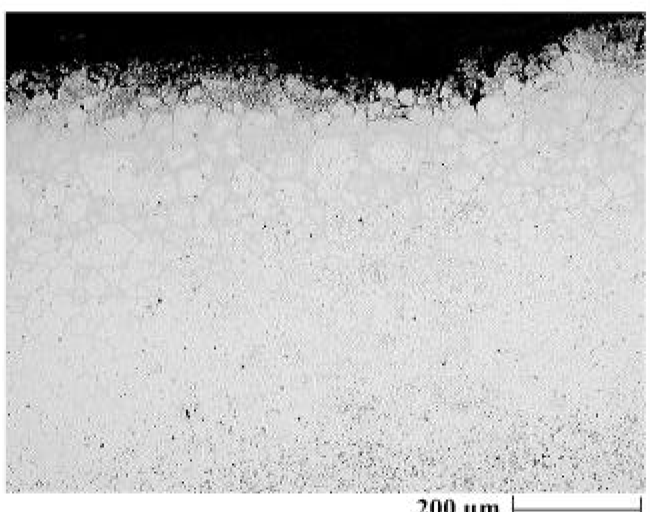


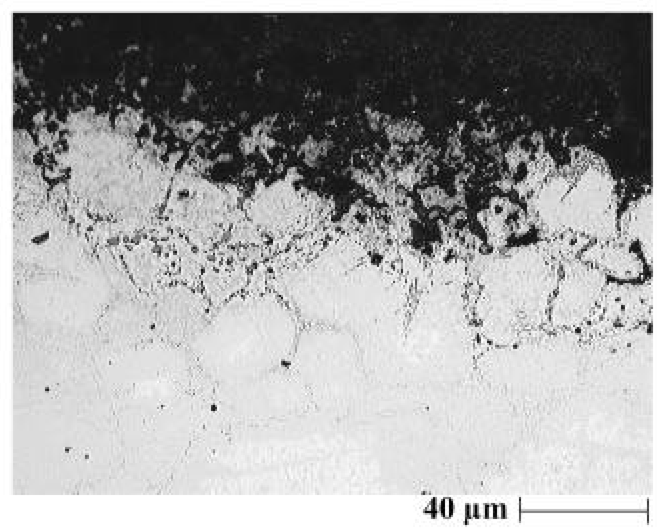
Modified Coal-Ash Corrosion Of Stainless Steels





Modified Coal-Ash Corrosion Of Stainless Steels





Ash Chemistry

External Deposit Analysis

Element	*Weight %*
Iron	36.4
Oxygen	36.2
Chromium	6.8
Aluminum	7.5
Sulfur	0.6
Silicon	9.4
Manganese	0.4
Nickel	1.1
Magnesium	0.3
Potassium	0.7
Calcium	0.3
Titanium	0.3

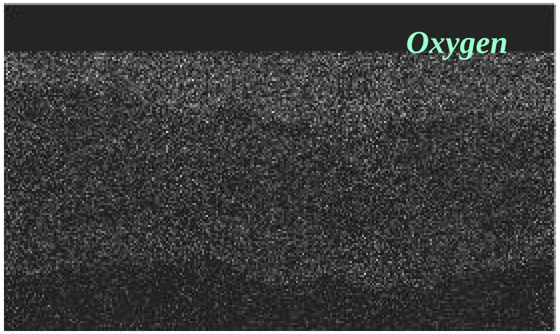
Hardness Increases Related to Surface Carburization

Hardness Measurement

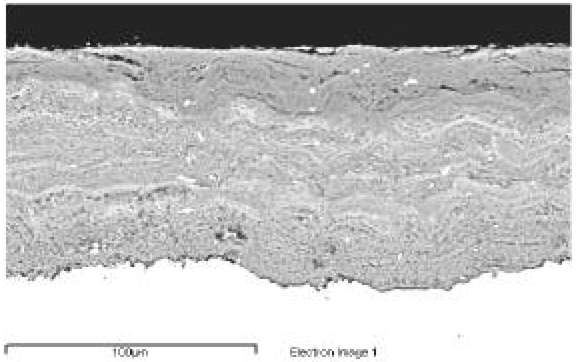
Sample		**HARDNESS VALUES-HV (HRB or HRC)**	
		Average	***Range***
RH Tubing	*Carburized Layer (Extrados Side)*	356 (36 HRC)	329 (33 HRC) – 402 (41 HRC)
	Extrados Side	222 (95 HRB)	218 (95 HRB) – 225 (96 HRB)
	Intrados Side	194 (90 HRB)	192 (90 HRB) – 197 (90 HRB)

Second Example of Modified Coal-Ash Corrosion Of Stainless Steels

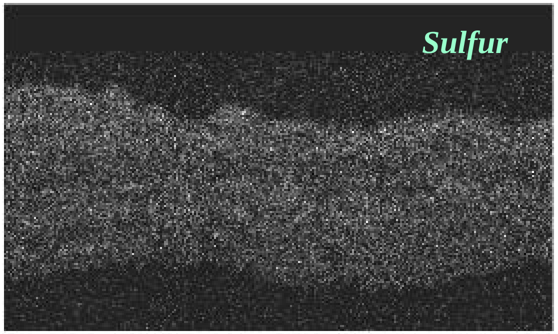
Element Distribution in Corrosion Product



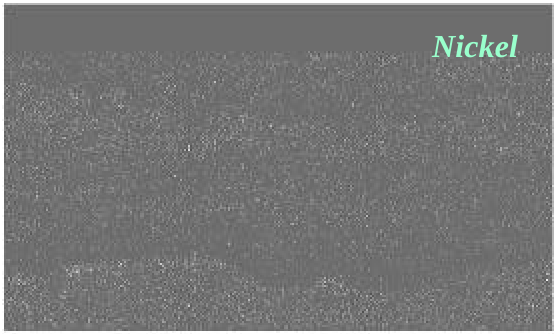
Oxygen Ka1



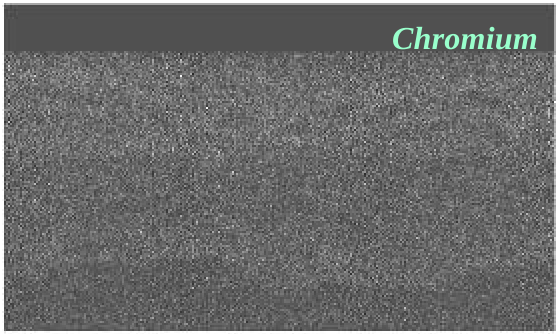
Electron Image 1



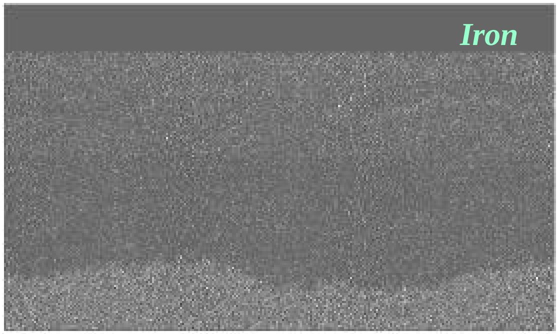
Sulfur Ka1



Nickel Ka1

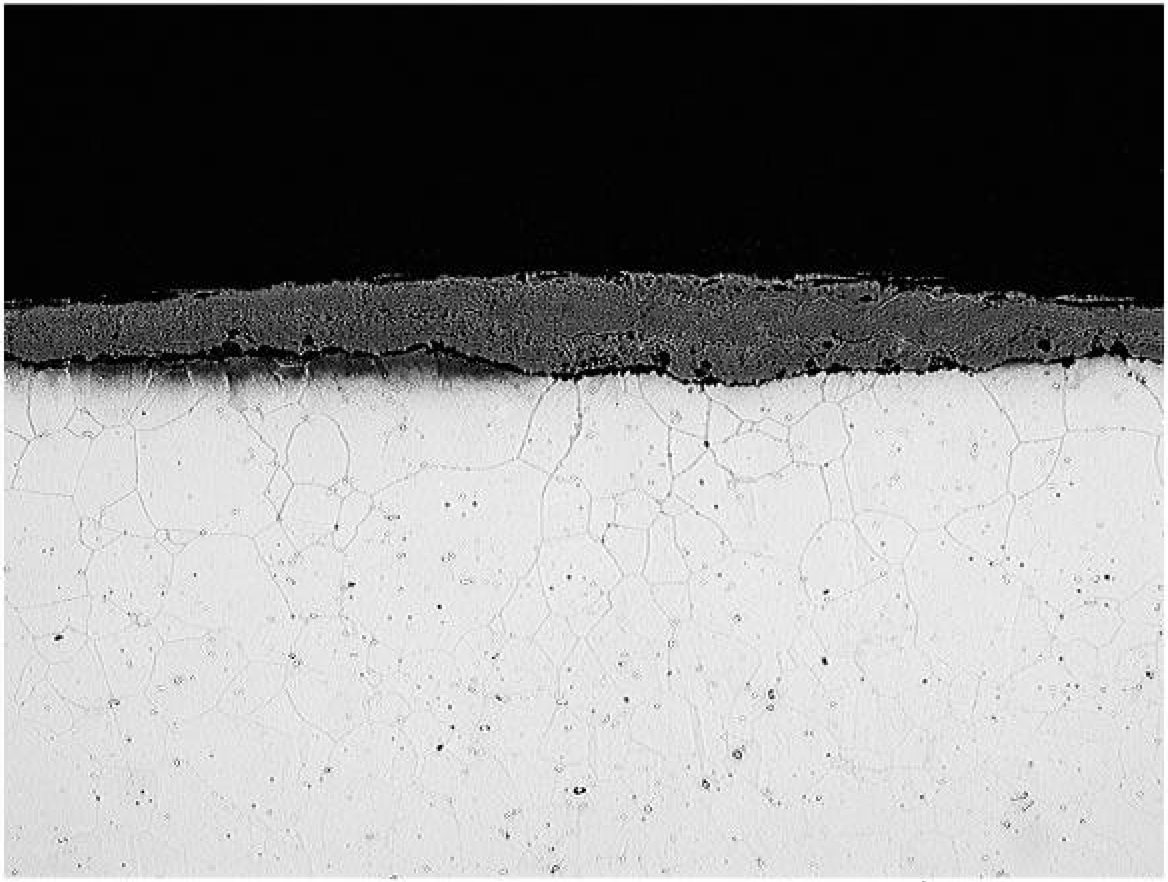


Chromium Ka1



Iron Ka1

Surface Carburization



200 µm

Mitigation Strategy for Modified Attack

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- **Response to This Problem--Apply More Highly Alloyed Materials Such As 45Cr-50Ni Alloy Without Fully Understanding Altered Boiler Environment and Corrosion Mechanism**
- **Weld Overlay or Thermal-Spray of 45Cr-50Ni**
- **Painful Cost Penalty--Tenfold Increase in Cost of Replacement RH Tubes Compared to Use of Original SS Material (Example)**

Example Of Weld Overlay

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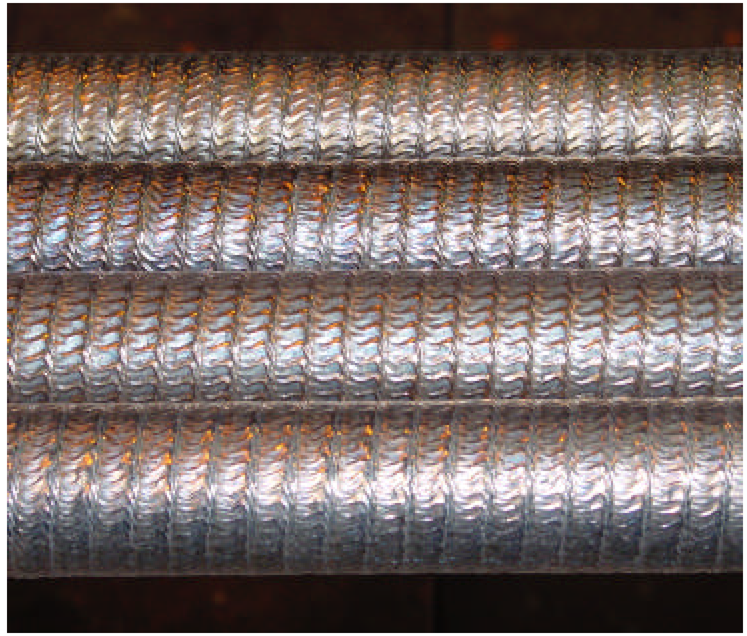

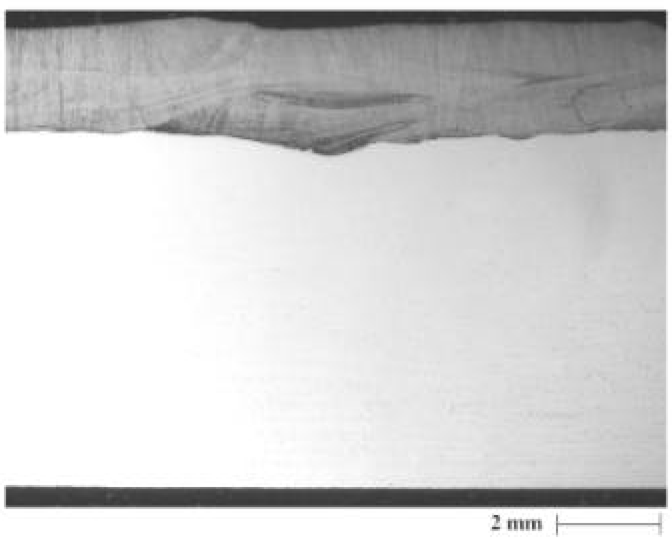

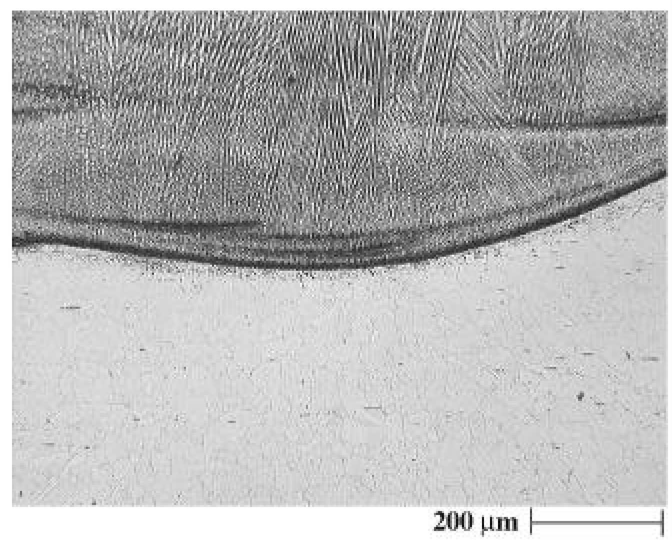

Better Technical Understanding Essential

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- It Is Imperative That a Better Understanding Be Gained of the Ways in Which Changes in Firing Conditions in Coal-fired Boilers Have Altered the Internal Environment of the Combustion Chamber and Subsequent Flue-Gas Passages.
- Proposals Have Been Made to DOE to Investigate This and Similar “New” Phenomena in Greater Depth.
- It Is Hoped That the Complex Links Between Boiler Operation, Fuel Chemistry, and Corrosion Behavior Will Be More Fully Understood So That Economic Solutions to the Corrosion Issue Can Be Identified.
- Only If Such an Understanding Is Gained Will It Be Possible to Operate the Next Generation of Coal-fired Boilers at Advanced Steam Conditions.