

API 571 - High Temperature Corrosion > 204 °C

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2013- API570 Examination	2013-API510 Examination
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Exam	Damage Mechanism	Temperatures	Affected materials
	4.4.1 oxidation	CS > 1000 °F SS > 1500 °F	All
510/570	4.4.2 Sulfidation	Iron based >500 °F	All iron based, Nickel based and copper based
	4.4.3 Carburization	> 1100 °F	All
	4.4.4 Decarburization		CS, low alloy steel
	4.4.5 Metal dusting	900 °F~ 1500 °F	All
	4.4.6 Fuel ash corrosion	700 °F/ 1000 °F/ 1130 °F	All
	4.4.7 Nitriding	Start: 600 °F Severe: 900 °F	All

High temperature corrosion

is a mechanism of corrosion that takes place in gas turbine, furnace or other machinery coming in contact with hot gas containing certain contaminants. Fuel sometimes contains vanadium compounds or sulfates which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high temperature corrosions include high temperature oxidation, sulfidation and carbonization.



4.4 High Temperature Corrosion [$>400^{\circ}\text{F}$ (204°C)]

- 4.4.1 Oxidation
- 4.4.2 Sulfidation
- 4.4.3 Carburization
- 4.4.4 Decarburization
- 4.4.5 Metal Dusting
- 4.4.6 Fuel Ash Corrosion
- 4.4.7 Nitriding

Mechanical and Metallurgical Failure Mechanisms

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Exam	Damage Mechanism	Temperatures	Affected materials
	Graphitisation	800°F~1100°F for C Steel 875°F for C ½ Mo Steel	Plain carbon steel C, C ½ Mo
	Spheroidisation	850 °F ~ 1400 °F	Low alloy steel up to 9% Cr
510	Tempered Embrittlement	650 °F~ 1070 °F	2 ¼ Cr-1Mo low alloy steel, 3Cr-1Mo (lesser extent), & HSLA Cr-Mo-V rotor steels
	Strain Aging	Intermediate temperature	Pre-1980's C-steels with a large grain size and C- ½ Mo
	885°F embrittlement	600 °F~ 1000 °F	300, 400 & Duplex SS containing ferrite phases

Exam	Damage Mechanism	Temperatures	Affected materials
	Sigma-Phase Embrittlement	1000 °F~ 1700 °F	Ferritic, austenitic & duplex SS.
510/570	Brittle Fracture	Below DTBTT	C, C- ½ Mo, 400 SS
	Creep & stress rupture	700 °F ~ 1000 °F	All metals and alloys
510/570	Thermal fatigues	Operating temperature	All materials of construction
	Short Term Overheating – Stress Rupture	>1000 °F	All fired heater tube materials and common materials of construction
	Steam Blanketing	>1000 °F	Carbon steel and low alloy steels
	Dissimilar Metal Weld (DMW) Cracking	Operating temperature	Carbon steel / 300 SS junction

Exam	Damage Mechanism	Temperatures	Affected materials
	Thermal Shock	Cold liquid impinge on hot surface	All metals and alloys.
570/510	Erosion/Erosion Corrosion	Service temperature	All
	Cavitation	Service temperature	All
570/510	Mechanical fatigue	Service temperature	All
570	Vibration-Induced Fatigue	Service temperature	All
	Refractory Degradation	Service temperature	All
	Reheat Cracking	Service temperature	CS, 300SS, Ni Based
	GOX enhances combustion	Service temperature	All

High Temperature Corrosion [$>400^{\circ}\text{F}$ (204°C)]

Exam	Damage Mechanism	Temperatures	Affected materials
	Oxidation	CS - $>1000^{\circ}\text{F}$ (538°C) 300SS- $>1500^{\circ}\text{F}$ (816°C).	CS, 300/400SS, Ni alloys
510/570	Sulfidation	Iron based alloy 500°F (260°C).	All metals and alloys
	Carburization	$>1100^{\circ}\text{F}$ (593°C)	All metals and alloys
	Decarburization	?	CS and low alloy steel
	Metal dusting	$900^{\circ}\text{F} \sim 1500^{\circ}\text{F}$ ($482^{\circ}\text{C} \sim 816^{\circ}\text{C}$)	All metals and alloys
	Fuel ash corrosion	$> 700^{\circ}\text{F}$ (371°C), varies with melting point of salts formed.	All metals and alloys
	Nitriding	$>600^{\circ}\text{F}$ (316°C)	Carbon steels, low alloy steels, 300 Series SS and 400 Series SS

4.4.1 Oxidation

4.4.1.1 Description of Damage

- a) Oxygen reacts with carbon steel and other alloys at high temperature converting the metal to oxide scale.
- b) It is most often present as oxygen is in the surrounding air (approximately 20%) used for combustion in fired heaters and boilers.

4.4.1.2 Affected Materials

- a) All iron based materials including carbon steel and low alloy steels, both cast and wrought.
- b) All 300 Series SS, 400 Series SS and nickel base alloys also oxidize to varying degrees, depending on composition and temperature.

4.4.1.3 Critical Factors

- a) The primary factors affecting high temperature oxidation are metal temperature and alloy composition.
- b) Oxidation of carbon steel begins to become significant above about 1000°F (538°C). Rates of metal loss increase with increasing temperature.
- c) In general, the resistance of carbon steel and other alloys is determined by the chromium content of the material. Increasing chromium levels produce a more protective oxide scale. The 300 Series SS are resistant to scaling up to about 1500°F (816°C). See Table 4-8.
- d) The presence of water vapor can significantly accelerate oxidation rates of some steels including 9Cr-1Mo (Reference 4.)



Table 4-8 – Estimated Corrosion Rates (mpy) for Oxidation (Reference 1).

[illegible][illegible]

Material	Maximum Metal Temperature (°F)											
	1525	1575	1625	1675	1725	1775	1825	1875	1925	1975	2025	2075
CS	--	--	--	--	--	--	--	--	--	--	--	--
1 1/4 Cr	--	--	--	--	--	--	--	--	--	--	--	--
2 1/4 Cr	--	--	--	--	--	--	--	--	--	--	--	--
5 Cr	--	--	--	--	--	--	--	--	--	--	--	--
7 Cr	--	--	--	--	--	--	--	--	--	--	--	--
9 Cr	60	--	--	--	--	--	--	--	--	--	--	--
12 Cr	50	--	--	--	--	--	--	--	--	--	--	--
304 SS	6	9	13	18	25	35	48	--	--	--	--	--
309 SS	4	6	8	10	13	16	20	30	40	50	--	--
310 SS / HK	3	4	5	7	8	10	13	15	19	23	27	31
800 H / HP	3	4	6	8	10	13	17	21	27	33	41	50

4.4.1.4 Affected Units or Equipment

Oxidation occurs in fired heaters and boilers as well as other combustion equipment, piping and equipment that operates in high temperature environments when metal temperatures exceed about 1000°F (538°C).

4.4.1.5 Appearance or Morphology of Damage

- a) Most alloys, including carbon steels and low alloy steels, suffer general thinning due to oxidation. Usually, the component will be covered on the outside surface with an oxide scale, depending on the temperature and exposure time (Figure 4-111 to 4-113).
- b) 300 Series SS and nickel alloys generally have a very thin dark scale unless exposed to extremely high temperatures where metal loss rates are excessive.

4.4.1.6 Prevention / Mitigation

- a) Resistance to oxidation is best achieved by upgrading to a more resistant alloy.
- b) Chromium is the primary alloying element that affects resistance to oxidation. Other alloying elements, including silicon and aluminum, are effective but their concentrations are limited due to adverse affects on mechanical properties. They are often used in special alloys for applications such as heater supports, burner tips and components for combustion equipment.

4.4.1.7 Inspection and Monitoring

- a) Process conditions should be monitored for establishing trends of high temperature equipment where oxidation can occur.
- b) Temperatures can be monitored through the use of tubeskin thermocouples and/or infrared thermography.
- c) Loss in thickness due to oxidation is usually measured using external ultrasonic thickness measurements.

4.4.1.8 Related Mechanisms

Oxidation damage referred to in this section is due to surface scaling. Some damage mechanisms result in internal oxidation which is outside the scope of this document.

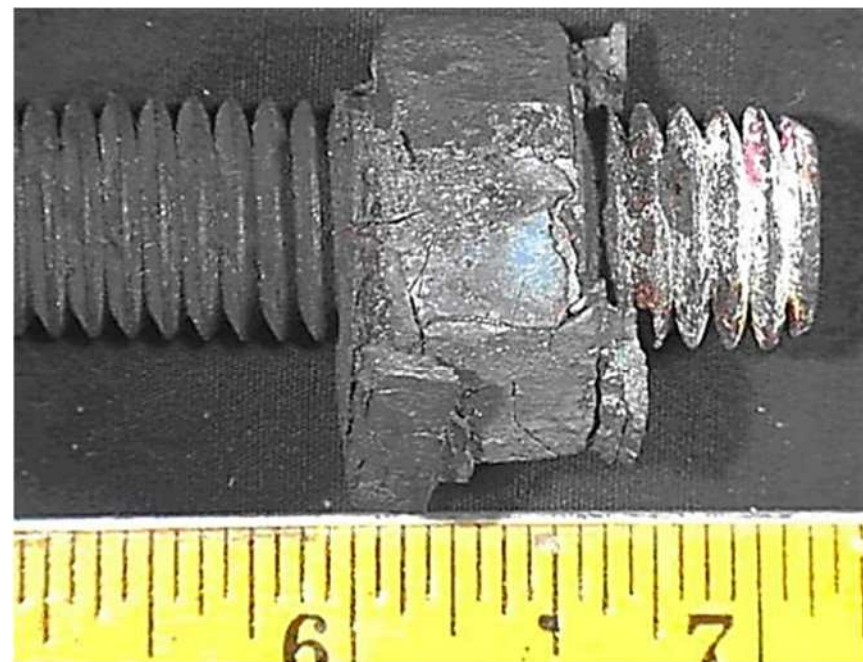


Figure 4-111 – Oxidation of a carbon steel nut on a stainless steel stud at 1300°F (704°C).

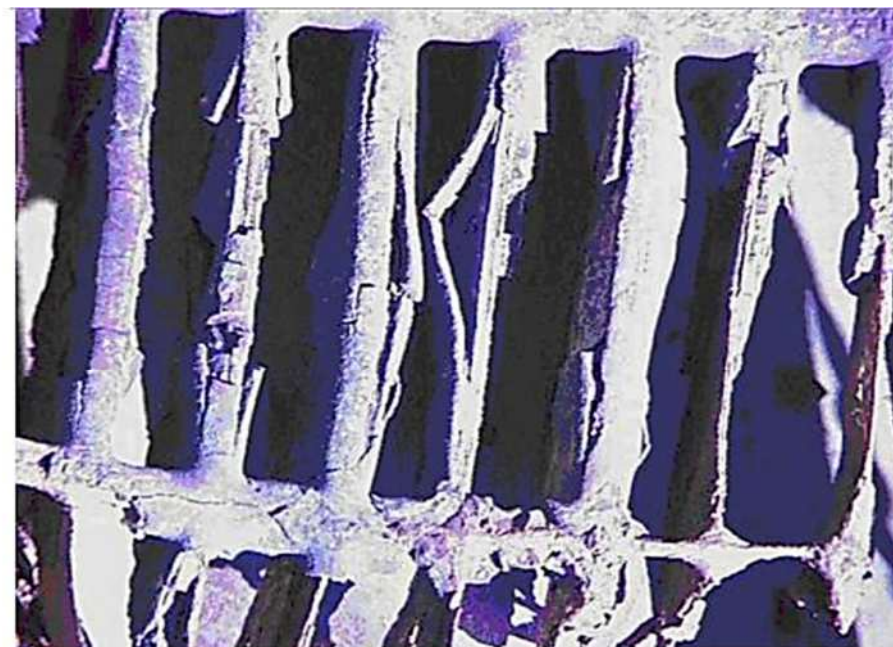


Figure 4-112 – Oxidation of a carbon steel grid from a sulfur reactor.



Figure 4-113 – Oxidation of the O.D. of a carbon steel furnace transfer line.

4.4.2 Sulfidation

4.4.2.1 Description of Damage

Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high temperature environments. **The presence of hydrogen accelerates corrosion.** This mechanisms is also known as sulfidic corrosion.

4.4.2.2 Affected Materials

- a) All iron based materials including carbon steel and low alloy steels, 300 Series SS and 400 Series SS.
- b) Nickel base alloys are also affected to varying degrees depending on composition, especially chromium content.
- c) Copper base alloys form sulfide at lower temperatures than carbon steel.

4.4.2.3 Critical Factors

- a) Major factors affecting sulfidation are alloy composition, temperature and concentration of corrosive sulfur compounds.
- b) Susceptibility of an alloy to sulfidation is determined by its ability to form protective sulfide scales.
- c) Sulfidation of iron-based alloys usually begins at metal temperatures above 500°F (260°C). The typical effects of increasing temperature, chromium content and sulfur content on metal loss are shown in Figure 4-114 and Figure115.

Note: These graphs are provided for reference only for general estimating of corrosion behavior and trends, and should not be used to make an exact determination of corrosion rates. The references at the end of this section should be consulted for additional background on the development of these curves.

- e) In general, the resistance of iron and nickel base alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 Series SS, such as Types 304, 316, 321 and 347, are highly resistant in most refining process environments. Nickel base alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation.
- f) Crude oils, coal and other hydrocarbon streams contain sulfur at various concentrations. Total sulfur content is made up of many different sulfur-containing compounds.
- g) Sulfidation is primarily caused by H_2S and other reactive sulfur species as a result of the thermal decomposition of sulfur compounds at high temperatures. Some sulfur compounds react more readily to form H_2S . Therefore, it can be misleading to predict corrosion rates based on weight percent sulfur alone.
- h) A sulfide scale on the surface of the component offers varying degrees of protection depending on the alloy and the severity of the process stream.

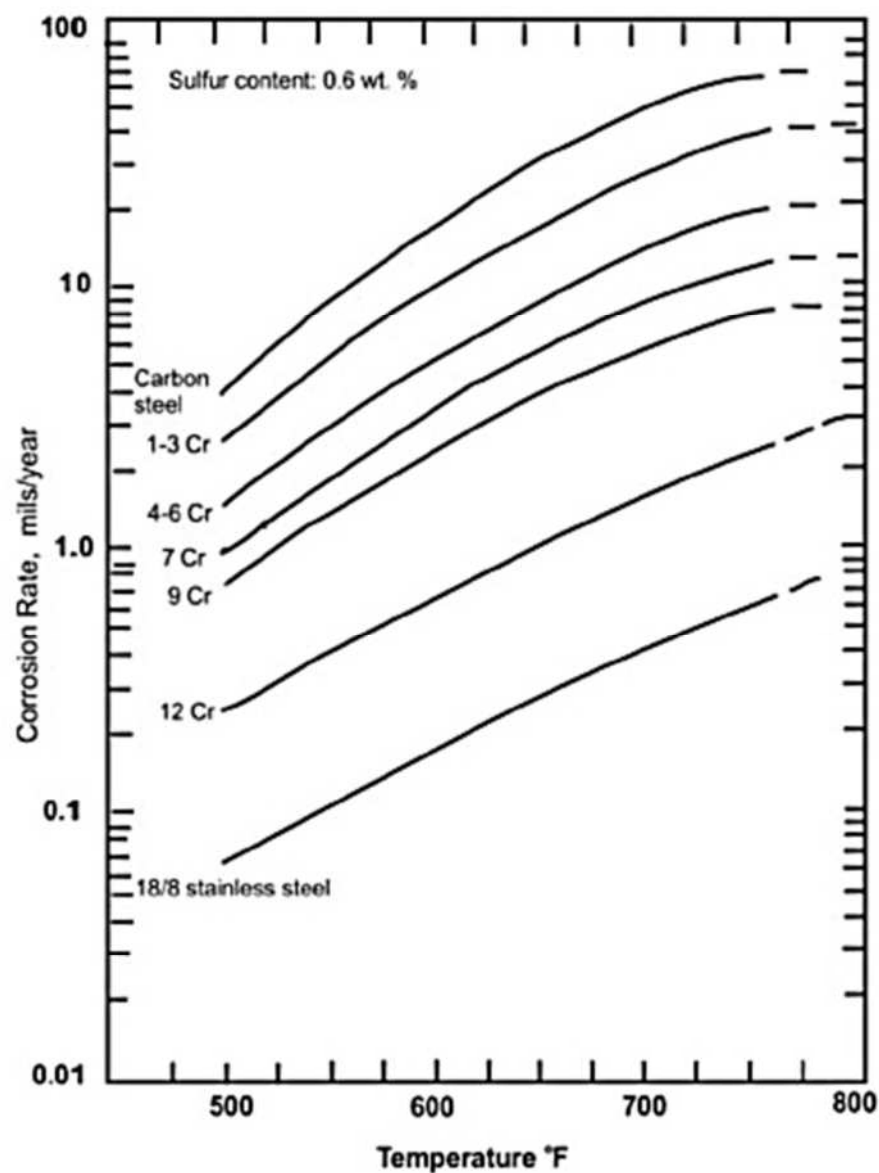


Figure 4-114 – Modified McConey curves showing typical effect of temperature on high temperature sulfidation of steels and stainless steels. (Reference 3)

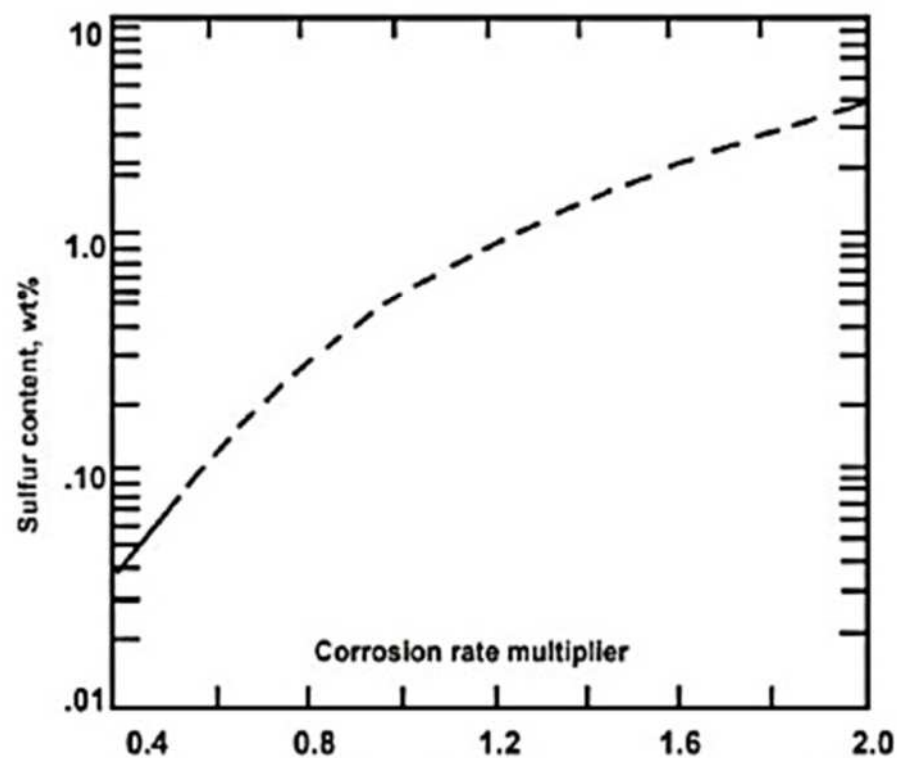


Figure 4-115 – Multiplier for corrosion rates in Figure 4-112 based on differing sulfur content of process fluid. (Reference 3)

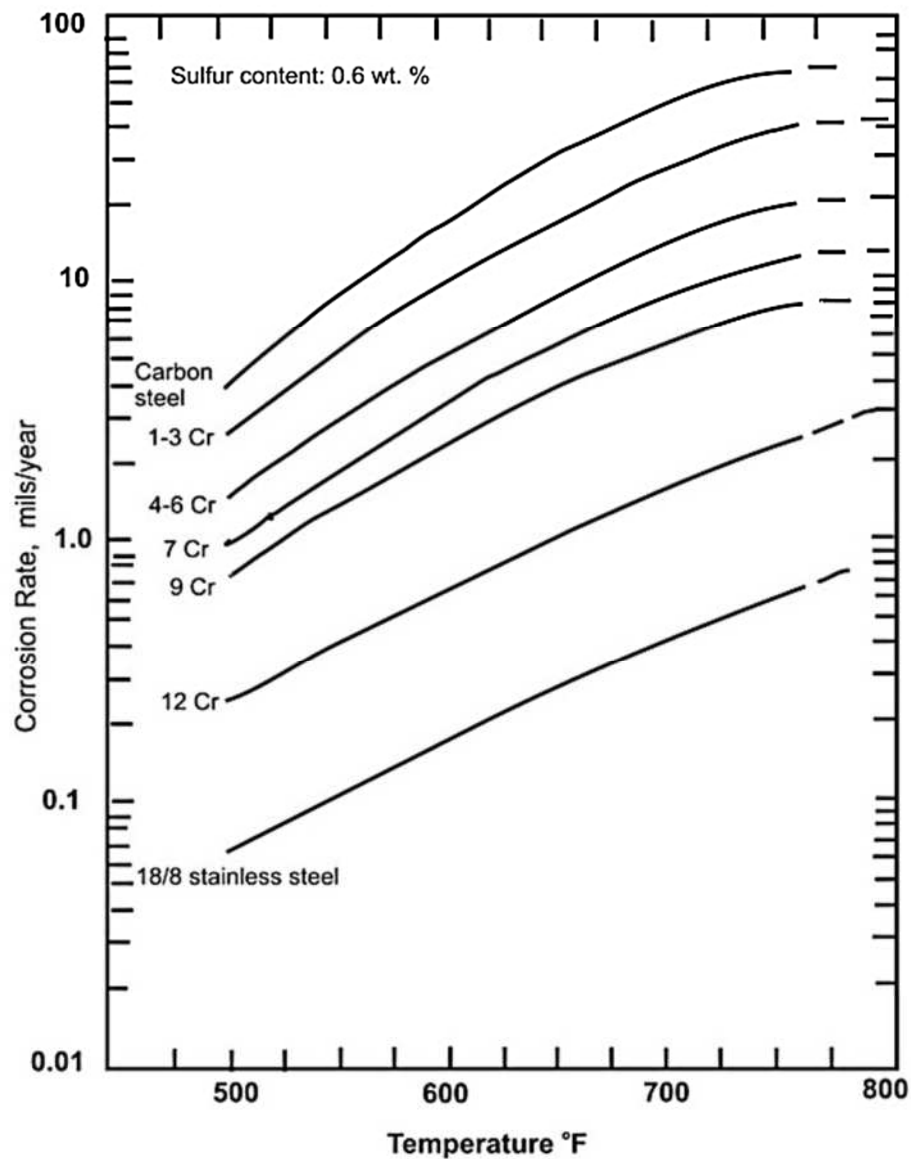


Figure 4-114 – Modified McCconomy curves showing typical effect of temperature on high temperature sulfidation of steels and stainless steels. (Reference 3)

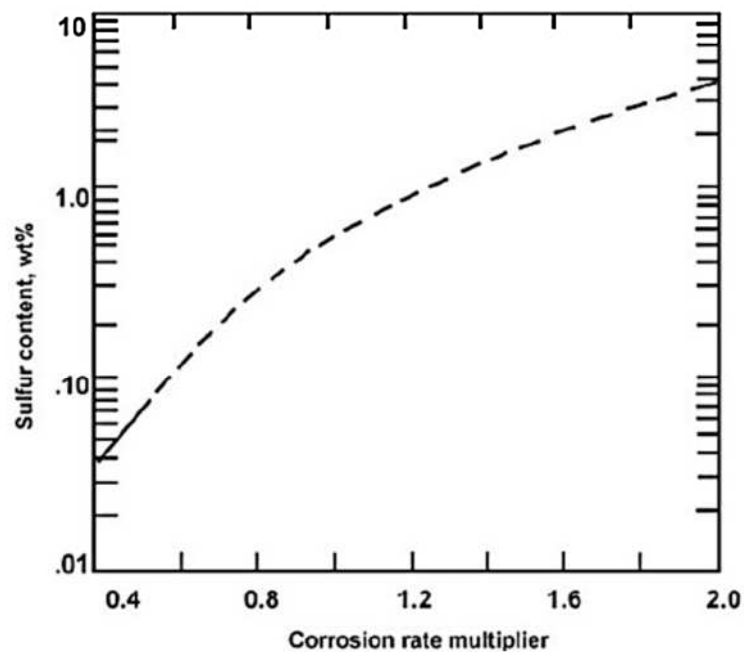


Figure 4-115 – Multiplier for corrosion rates in Figure 4-112 based on differing sulfur content of process fluid. (Reference 3)

4.4.2.4 Affected Units or Equipment

- a) Sulfidation occurs in piping and equipment in high temperature environments where sulfur-containing streams are processed.
- b) Common areas of concern are the crude, FCC, coker, vacuum, visbreaker and hydroprocessing units.
- c) Heaters fired with oil, gas, coke and most other sources of fuel may be affected depending on sulfur levels in the fuel.
- d) Boilers and high temperature equipment exposed to sulfur-containing gases can be affected.



4.4.2.5 Appearance or Morphology of Damage

- a) Depending on service conditions, corrosion is most often in the form of uniform thinning but can also occur as localized corrosion or high velocity erosion-corrosion damage (Figure 4-116 to 4-120).
- b) A sulfide scale will usually cover the surface of components. Deposits may be thick or thin depending on the alloy, corrosiveness of the stream, fluid velocities and presence of contaminants.

4.4.2.6 Prevention / Mitigation

- a) Resistance to sulfidation is generally achieved by upgrading to a higher chromium alloy.
- b) Piping and equipment constructed from solid or clad 300 Series SS or 400 Series SS can provide significant resistance to corrosion.
- c) Aluminum diffusion treatment of low alloy steel components is sometimes used to reduce sulfidation rates and minimize scale formation, however, it may not offer complete protection. 300 Series SS catalyst support screens in hydroprocessing reactors can also be treated to prolong life.

4.4.2.7 Inspection and Monitoring

- a) Process conditions should be monitored for increasing temperatures and/or changing sulfur levels.
- b) Temperatures can be monitored through the use of tubeskin thermocouples and/or infrared thermography.
- c) Evidence of thinning can be detected using external ultrasonic thickness measurements and profile radiography.
- d) Proactive and retroactive PMI programs are used for alloy verification and to check for alloy mix-ups in services where sulfidation is anticipated (Reference 7).

4.4.2.8 Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High temperature sulfidation in the presence of hydrogen is covered in 5.1.1.5.



Figure 4-116 – Sulfidation failure of NPS 8 carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.



Figure 4-117 – Sulfidation failure illustrating the effect of accelerated corrosion due to low silicon content. This 8 inch NPS pipe section in FCC bottoms piping was in service at 150 psig (1Mpa) at 650° to 700°F (340° to 370°C). The piping sketch in Figure 118 illustrates the difference in corrosion rate as compared to adjacent high-silicon components.

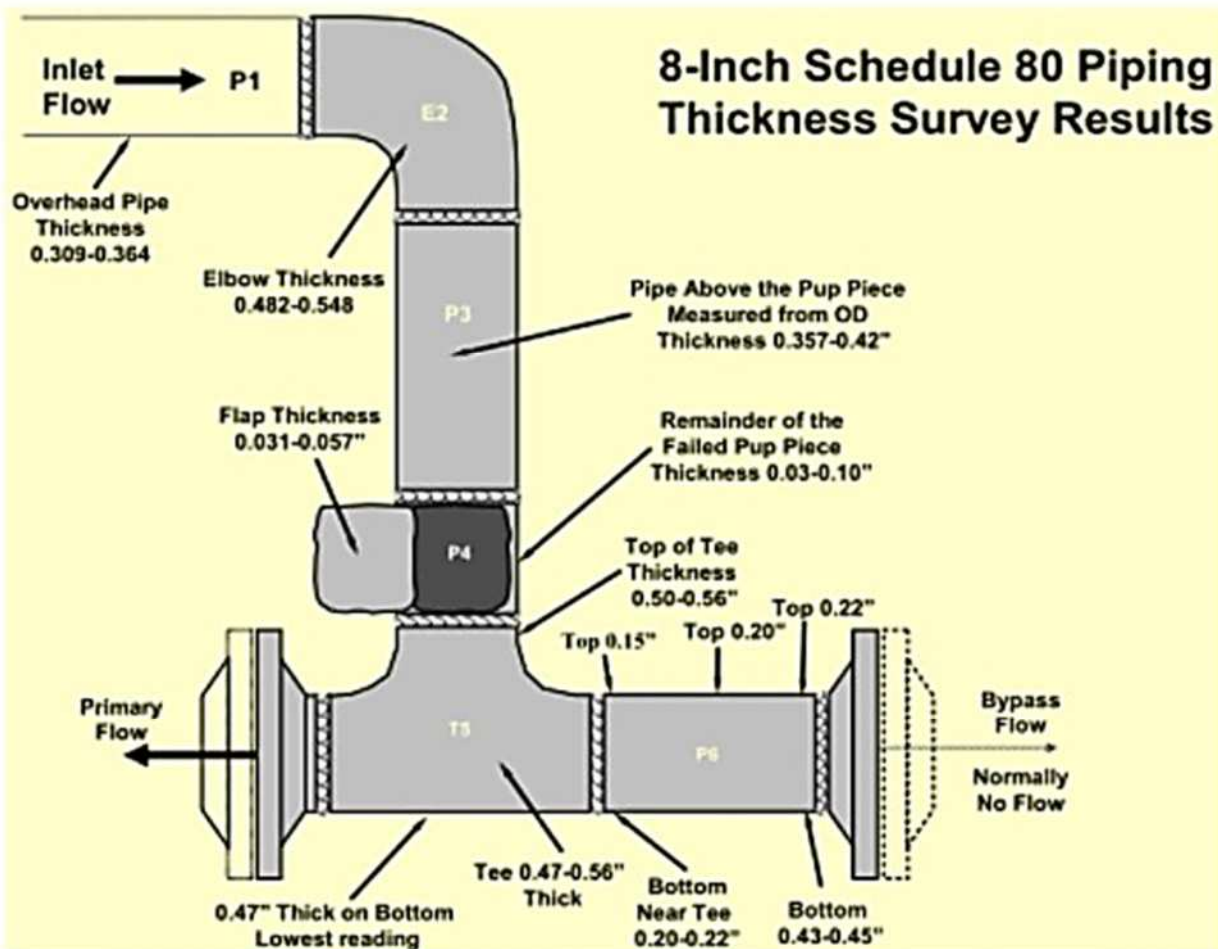


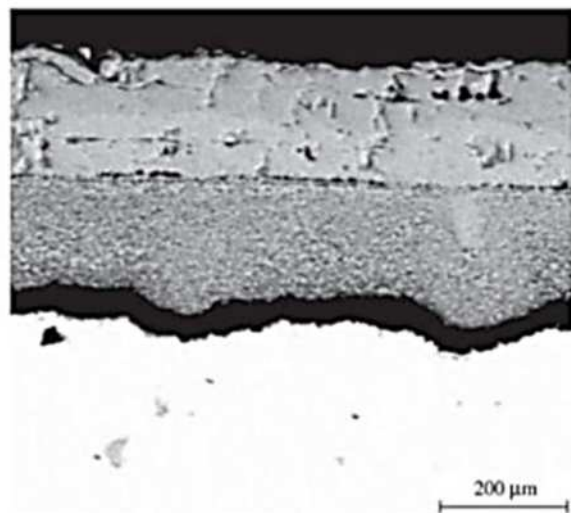
Figure 4-118 – Thickness survey of 8 inch pipe shown in Figure 4-117 above.



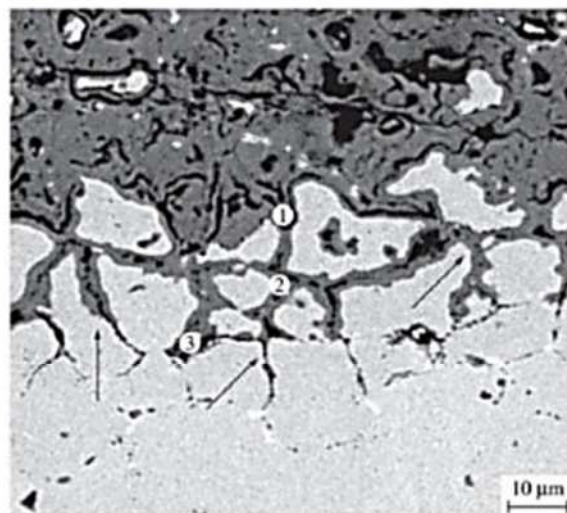
Figure 4-119 – Sulfidation failure of carbon steel sight glass nipple on the right after 2 years in crude unit. Original thickness is shown on left for comparison. Material was supposed to be 9Cr-1Mo.



Figure 4-120 – Sulfidation failure of piping elbow.

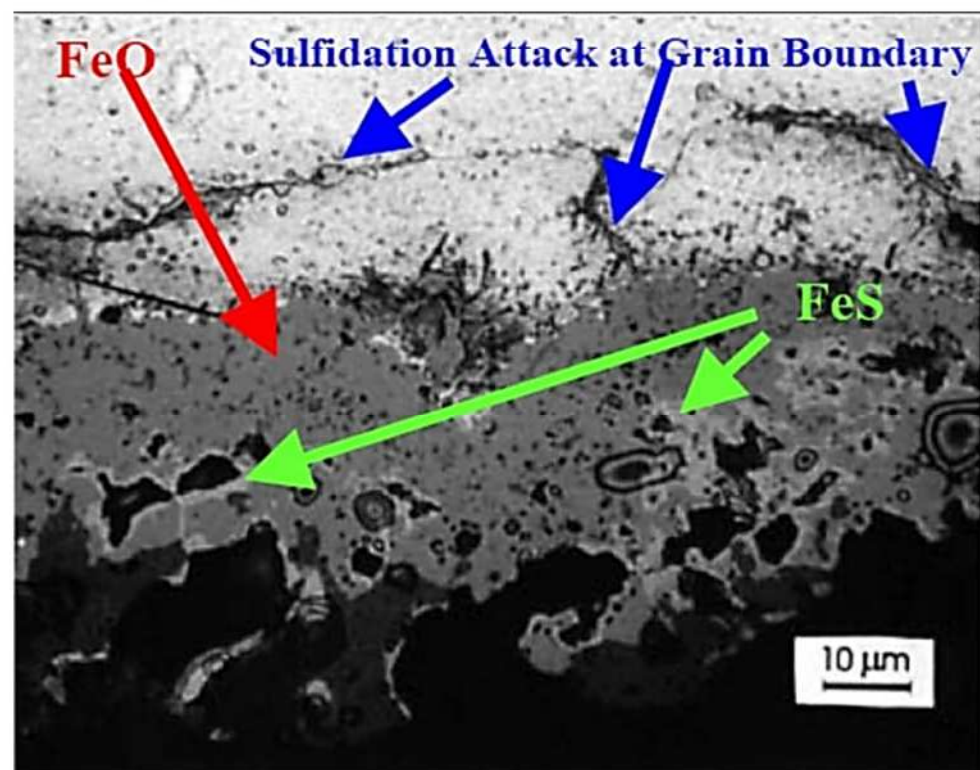


a)



b)

Figure 8. SEM cross-section of the G11 steel sample subjected to the simulated condition at 700 °C. a) General view of the corroded layer and substrate showing in detail the detachment of the layer from the substrate; b) Detail of the corroded layer/substrate interface, showing the internal oxidation and sulfidation.



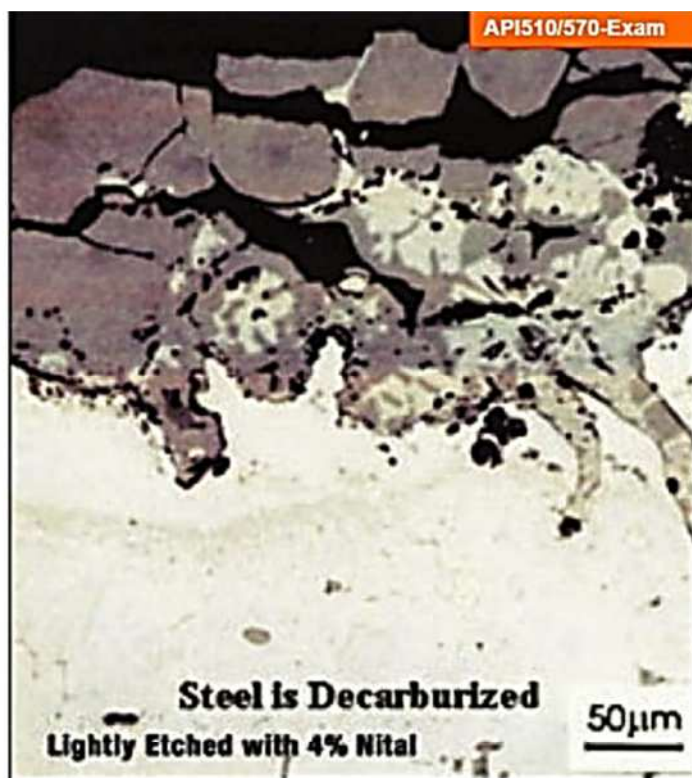
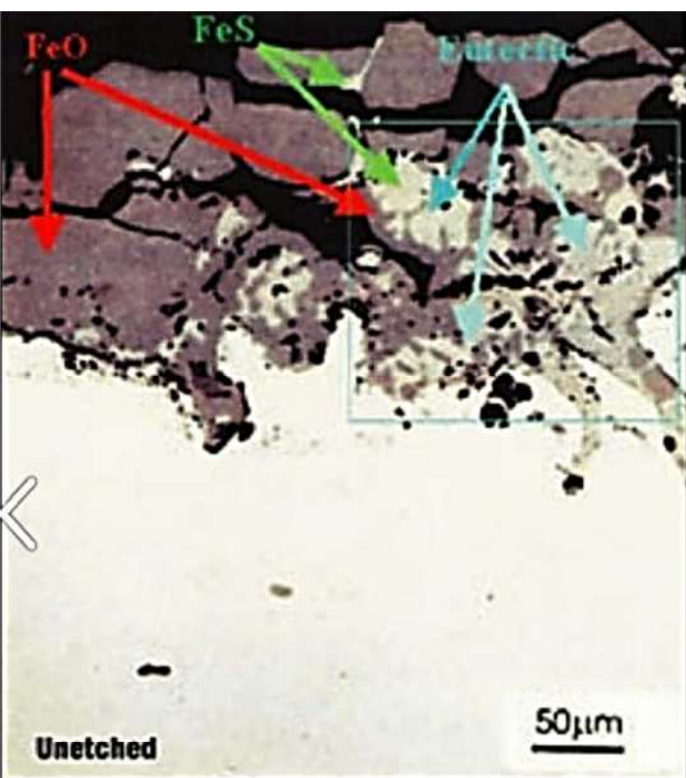
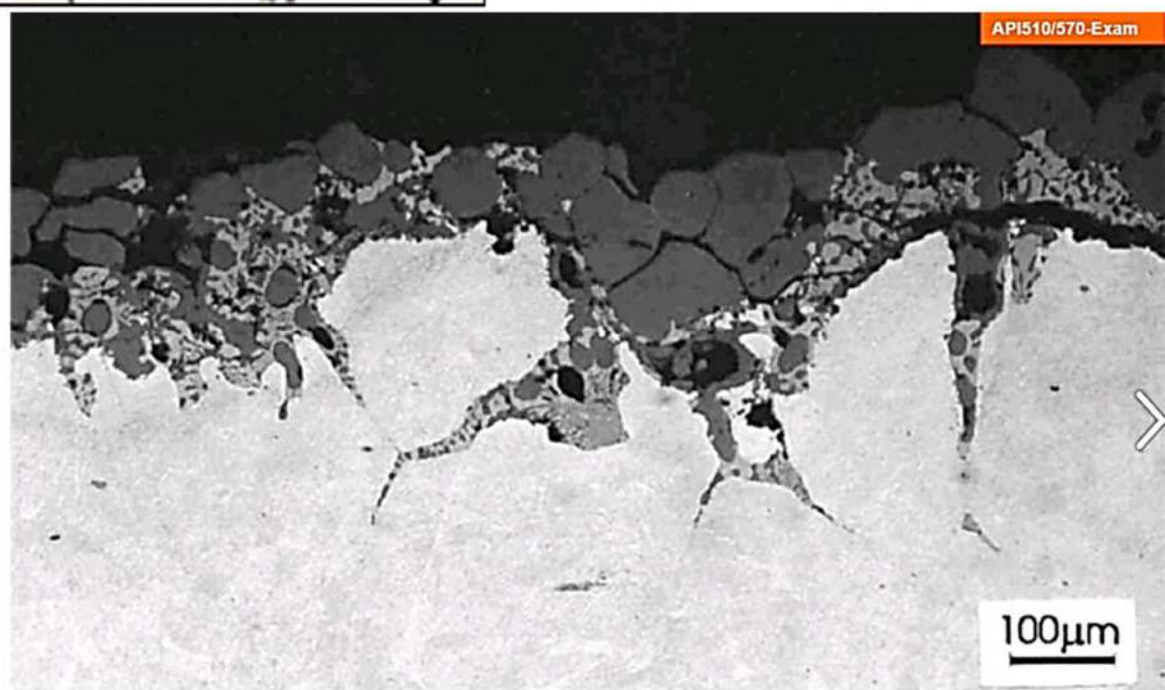


Figure C-4 Optical microstructure near the steel surface.





4.4.3 Carburization

4.4.3.1 Description of Damage

Carbon is absorbed into a material at elevated temperature while in contact with a carbonaceous material or carburizing environment.

4.4.3.2 Affected Materials

Carbon steel and low alloy steels, 300 Series SS and 400 Series SS, cast stainless steels, nickel base alloys with significant iron content (e.g., Alloys 600 and 800) and HK/HP alloys.

4.4.3.3 Critical Factors

a) Three conditions must be satisfied:

1. Exposure to a carburizing environment or carbonaceous material.
2. Temperature high enough to allow diffusion of carbon into the metal [typically above 1100°F (593°C)].
3. Susceptible material.

b) Conditions favoring carburization include a high gas phase carbon activity (hydrocarbons, coke, gases rich in CO, CO₂, methane, ethane) and low oxygen potential (minimal O₂ or steam).

- c) Initially, carbon diffuses into the component at a high rate and then tapers off as the depth of carburization increases.
- d) In carbon steels and low alloy steels, carbon reacts to form a hard, brittle structure at the surface that may crack or spall upon cooling.
- e) 300 Series SS are more resistant than carbon steel and the low alloy steels due to higher chromium and nickel content.
- f) Carburization can result in the loss of high temperature creep ductility, loss of ambient temperature mechanical properties (specifically toughness/ductility), loss of weldability, and corrosion resistance.

4.4.3.4 Affected Units or Equipment

- a) Fired heater tubes are the most common type of equipment susceptible to carburization in the environments mentioned earlier.
- b) Coke deposits are a source of carbon that may promote carburization, particularly during decoke cycles where temperatures exceed the normal operating temperatures, accelerating the carburization.
- c) Carburization is sometimes found in heater tubes in catalytic reformers and coker units or other heaters where steam/air decoking is performed.
- d) Carburization is also encountered in ethylene pyrolysis and steam reformer furnaces. Significant carburization occurs during decoking cycles.

4.4.3.5 Appearance or Morphology of Damage

- a) The depth of carburization can be confirmed by metallography. Figure 4-121 to 4-122.
- b) Carburization can be confirmed by substantial increases in hardness and loss in ductility.
- c) In a more advanced stage, there may be a volumetric increase in the affected component.
- d) A change (increase) in the level of ferromagnetism can occur in some alloys.
- e) Carburization results in the formation of metal carbides depleting the surrounding matrix of the carbide-forming element.

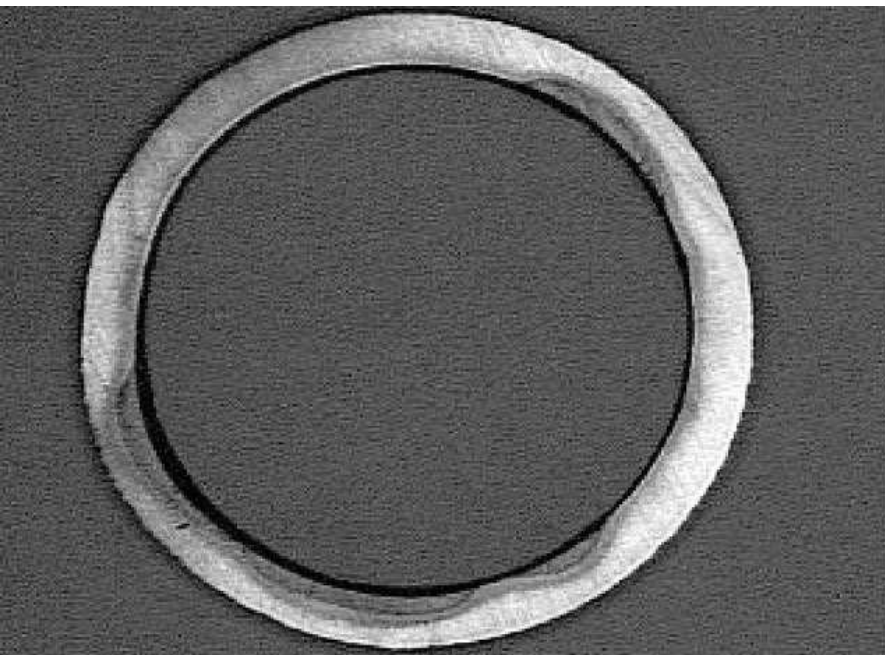


Figure 4-121 – Carburization (dark areas) of an HP-modified tube from an ethylene furnace after 3 years at 1900°F (1038°C).

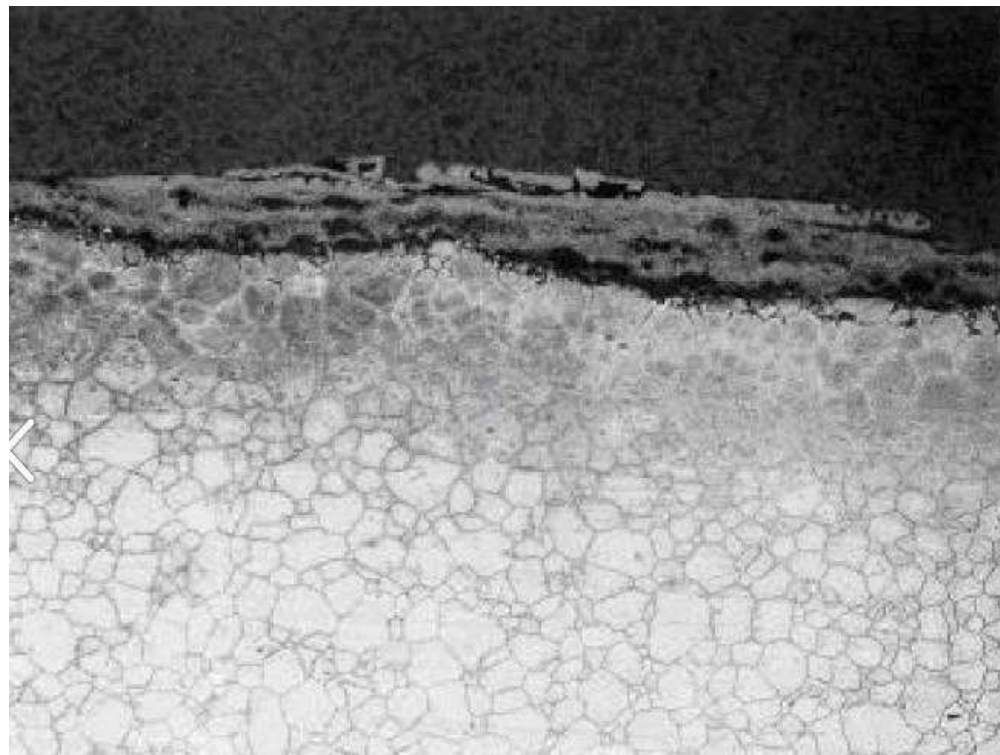


Figure 4-122 – A photomicrograph of a cross-section of a 304H cyclone from a fluid coker showing surface carburization after 24 years. Mag. 35X.



4.4.3.6 Prevention / Mitigation

- a) Select alloys with adequate resistance to carburization including alloys with a strong surface oxide or sulfide film formers (silicon and aluminum).
- b) Reduce the carbon activity of the environment through lower temperatures and higher oxygen/sulfur partial pressures. Sulfur inhibits carburization and is often added in the process stream in small amounts in steam/gas cracking in olefin and thermal hydro-dealkylation units.

4.4.3.7 Inspection and Monitoring

- a) Inspection for carburization in the initial stages of attack is difficult. If the process side surfaces are accessible, hardness testing and field metallography can be used. Destructive sampling and magnetic based techniques (Eddy Current) have also been used.
- b) Inspection techniques based on determining increased levels of ferromagnetism (magnetic permeability) are also useful for alloys that are paramagnetic when initially installed (austenitic alloys). However, surface oxides may interfere with the results.
- c) In the advanced stages of carburization where cracking has initiated, RT, UT and some magnetic techniques may be used.

4.4.3.8 Related Mechanisms

A severe form of carburization known as metal dusting is discussed in 4.4.5.

4.4.4 Decarburization

4.4.4.1 Description of Damage

A condition where steel loses strength due the removal of carbon and carbides leaving only an iron matrix. Decarburization occurs during exposure to high temperatures, during heat treatment, from exposure to fires, or from high temperature service in a gaseous environment.

4.4.4.2 Affected Materials

Carbon steels and low alloy steels.

4.4.4.3 Critical Factors

- a) Time, temperature and carbon activity of the process stream are the critical factors.
- b) The material must be exposed to a gas phase that has a low carbon activity so that carbon in the steel will diffuse to the surface to react with gas phase constituents.
- c) The extent and depth of decarburization is a function of the temperature and exposure time.
- d) Typically, shallow decarburization can slightly decrease the strength of the material, but has no detrimental effect on the overall performance of the component. However, it is indicative that the steel may have been overheated and suggests other effects may be present (e.g. decarburization associated with HTHA in hydrogen services).
- e) Potential loss in room temperature tensile strength and creep strength may occur.

4.4.4.4 Affected Units or Equipment

- a) Decarburization can occur in almost any equipment that is exposed to elevated temperatures, heat treated or exposed to a fire.
- b) Piping and equipment in hot hydrogen service in hydroprocessing units or catalytic reforming units as well as fired heater tubes can be affected. Pressure vessel components that are hot formed during fabrication can be affected.

4.4.4.5 Appearance or Morphology of Damage

- a) Damage can be verified by metallography.
- b) Damage occurs on the surface exposed to the gas environment but in extreme cases may be through wall.
- c) The decarburized layer will be free of carbide phases. Carbon steel will be pure iron (Figure 4-123 to 4-124).

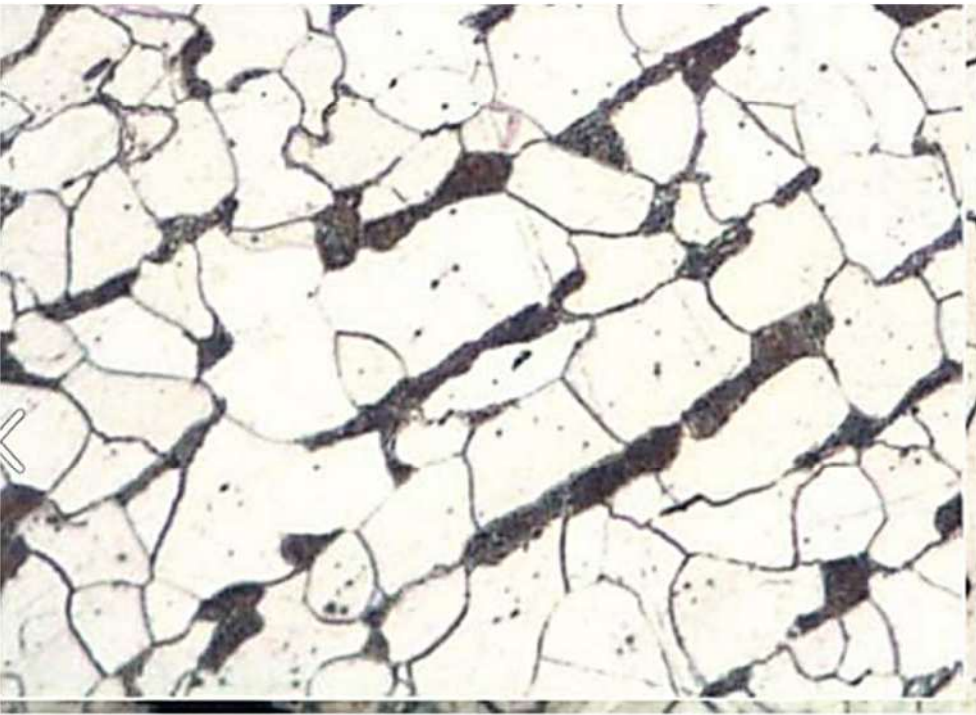


Figure 4-123 – Typical low carbon steel microstructure showing ferrite phase (light grains) and pearlite carbide (dark layered phases).

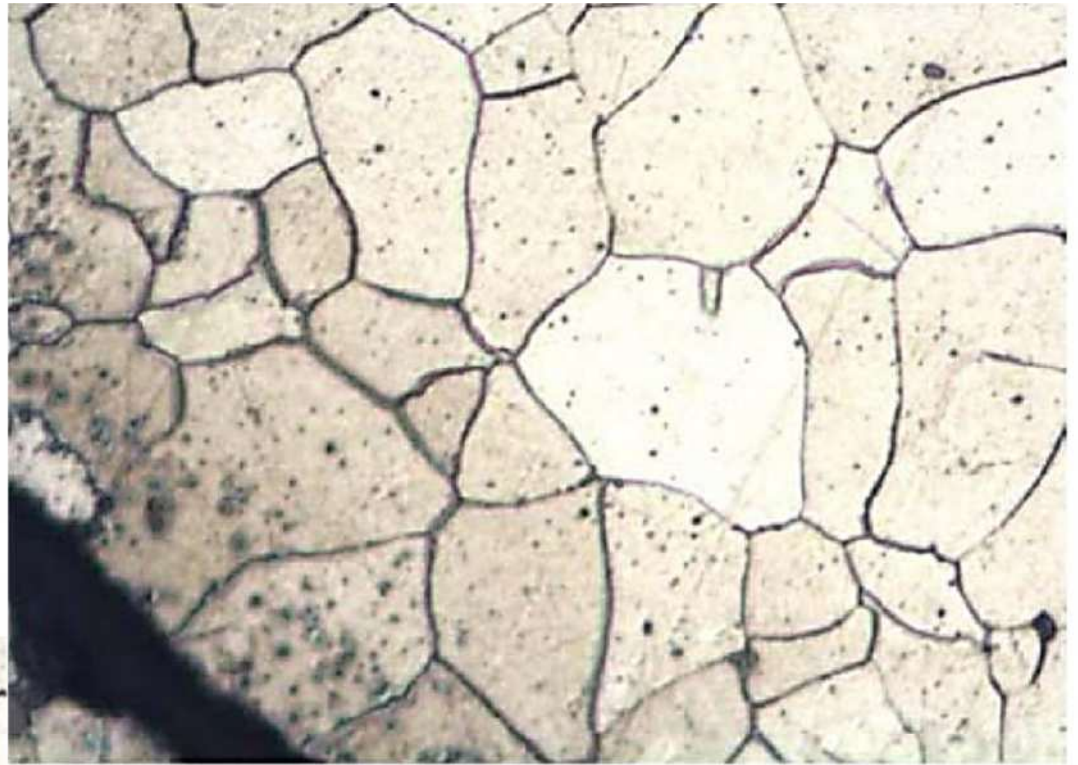


Figure 4-124 – Microstructure illustrating a decarburized low carbon steel where the strength providing pearlitic phases have been decomposed as a result of the removal of carbon atoms by diffusion to the surface.

4.4.4.6 Prevention / Mitigation

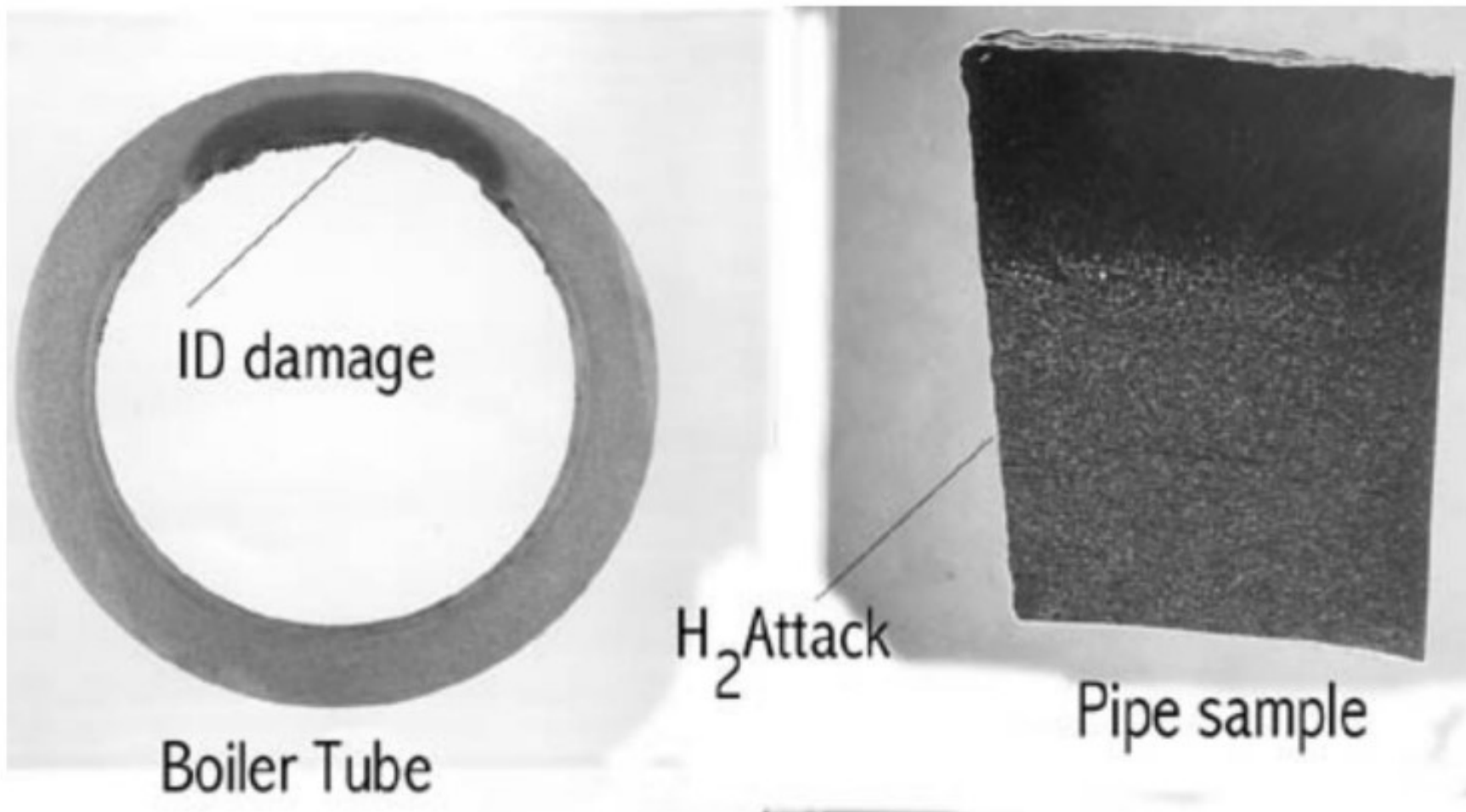
- a) Decarburization can be controlled by controlling the chemistry of the gas phase and alloy selection (API RP 941).
- b) Alloy steels with chromium and molybdenum form more stable carbides and are more resistant to decarburization.
- c) Steels operating in high temperature hydrogen environments should be selected in accordance with API RP 941.

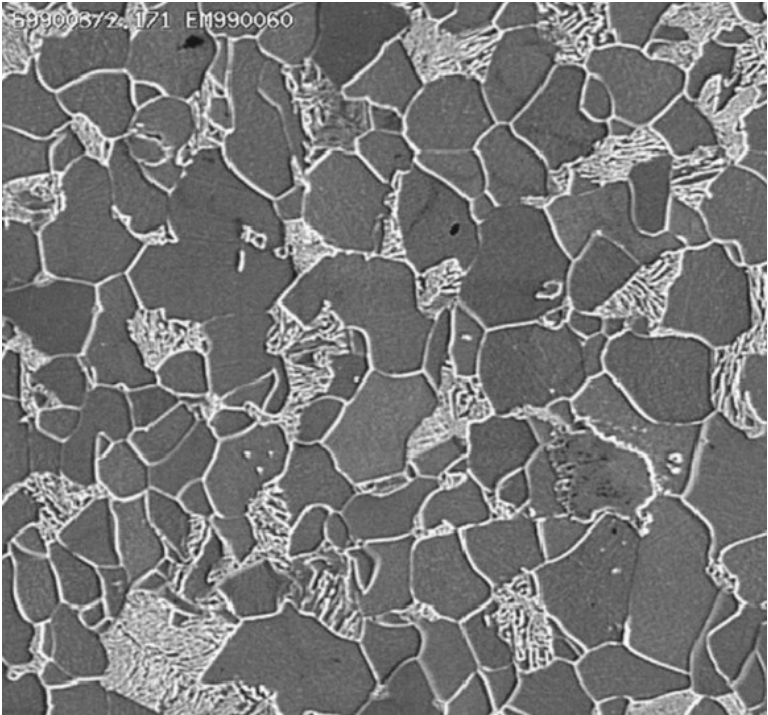
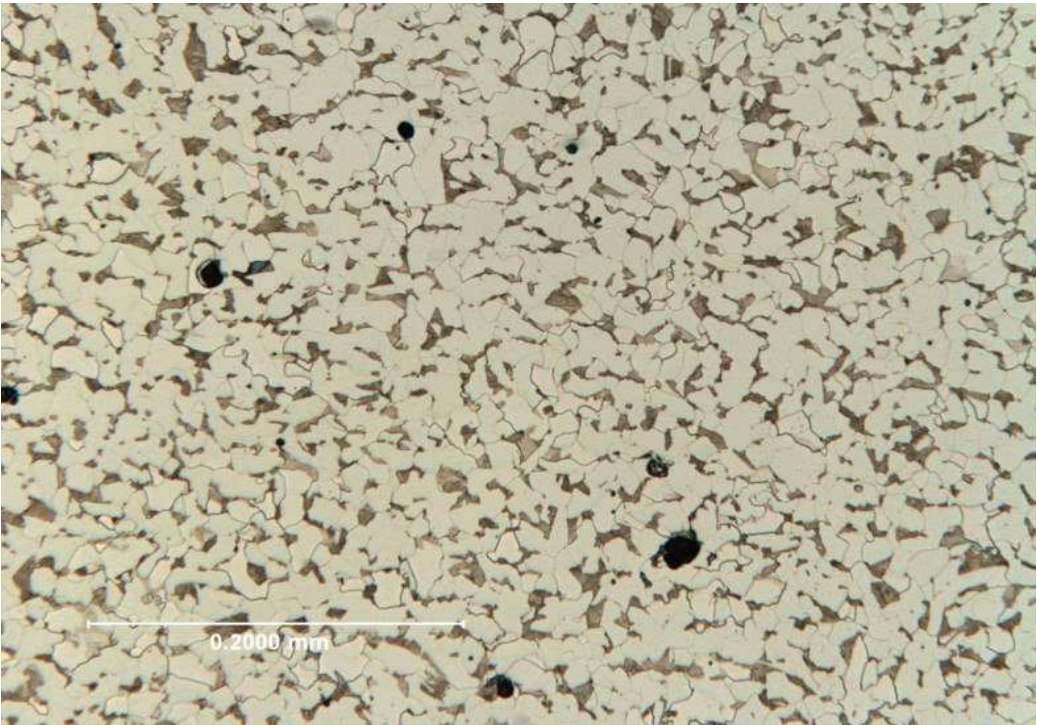
4.4.4.7 Inspection and Monitoring

- a) Field Metallography and Replication (FMR) can confirm decarburization.
- b) Decarburization results in a softening that can be confirmed by hardness testing.

4.4.4.8 Related Mechanisms

High Temperature Hydrogen Attack (HTHA) (see 5.1.3.1).





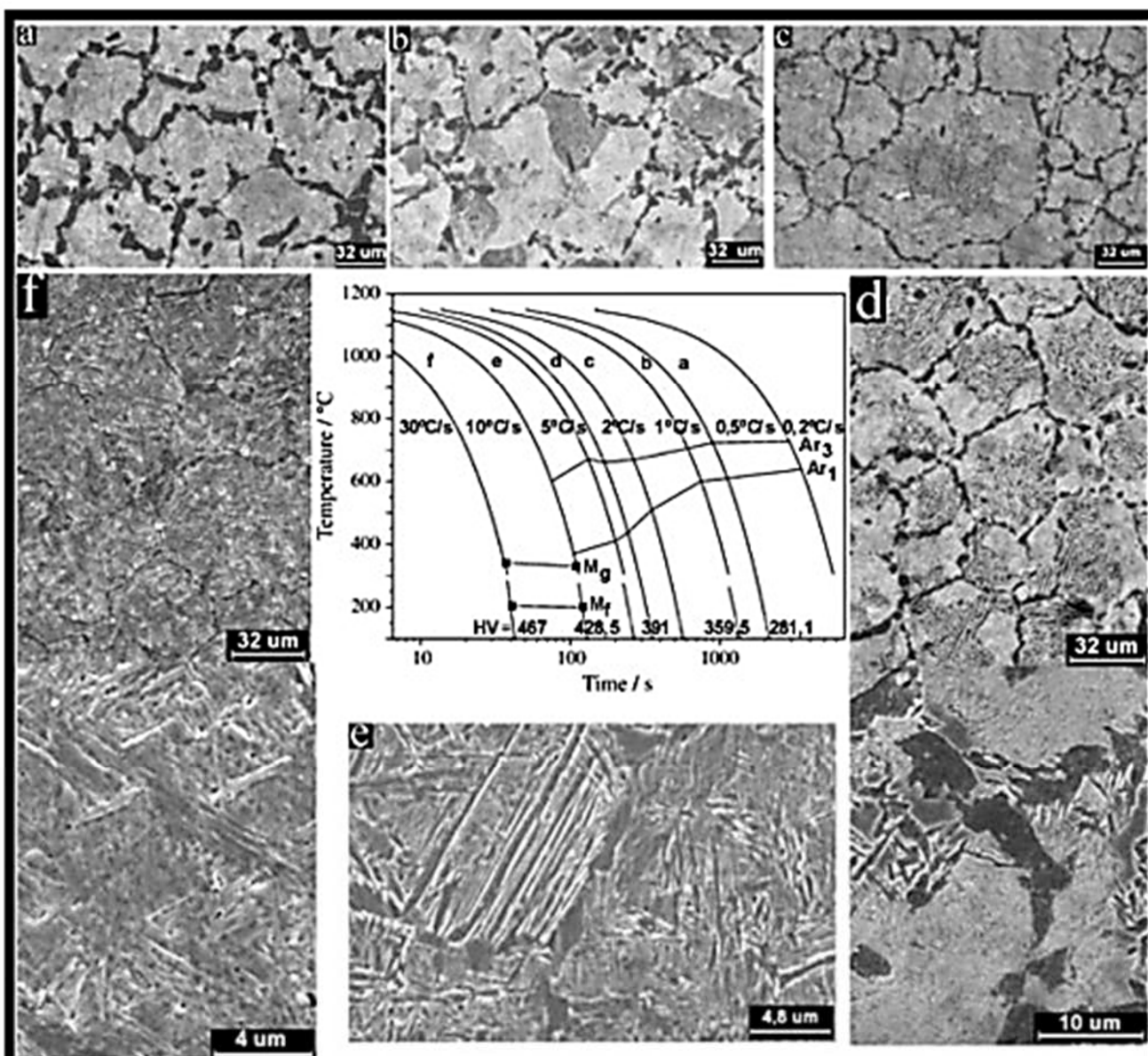
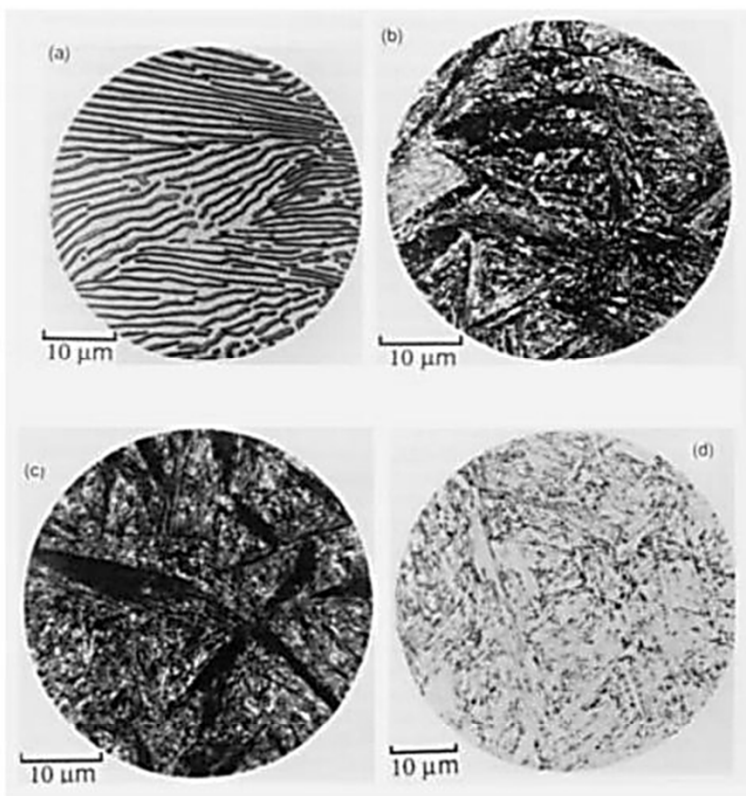
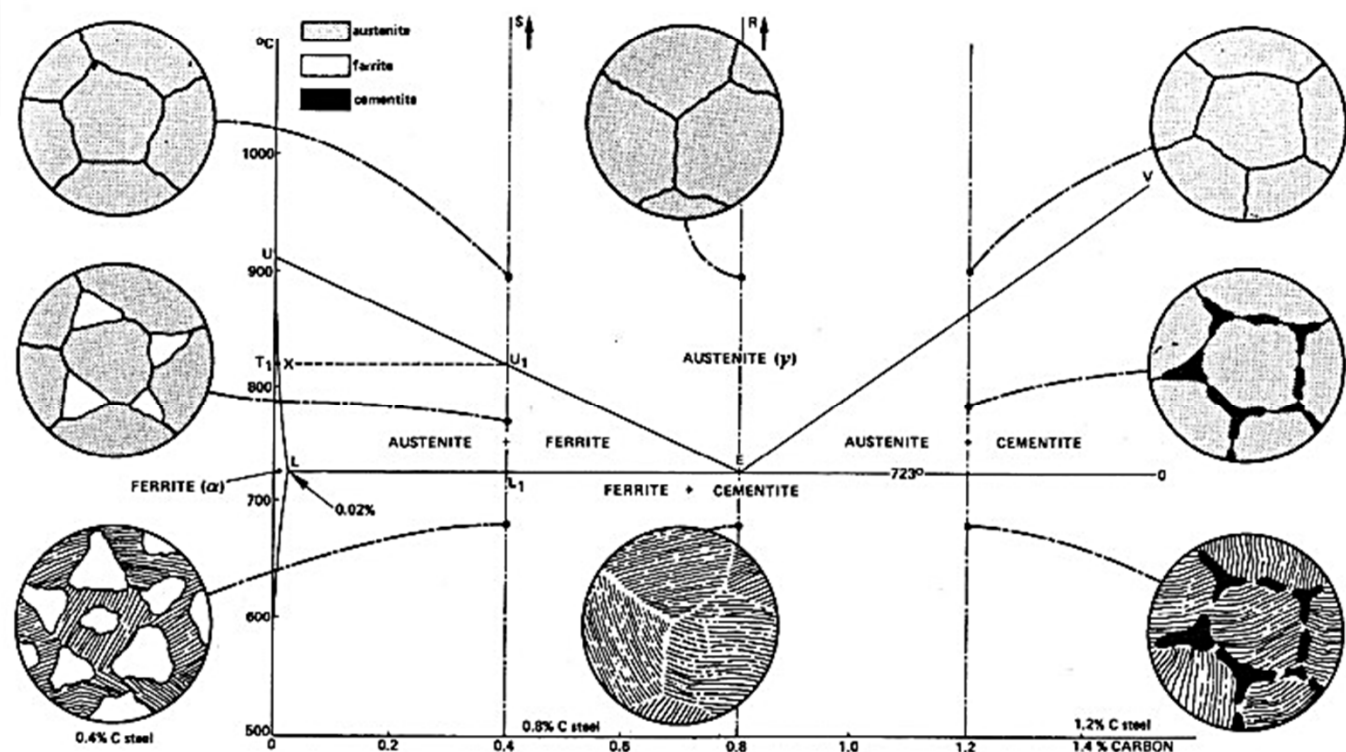
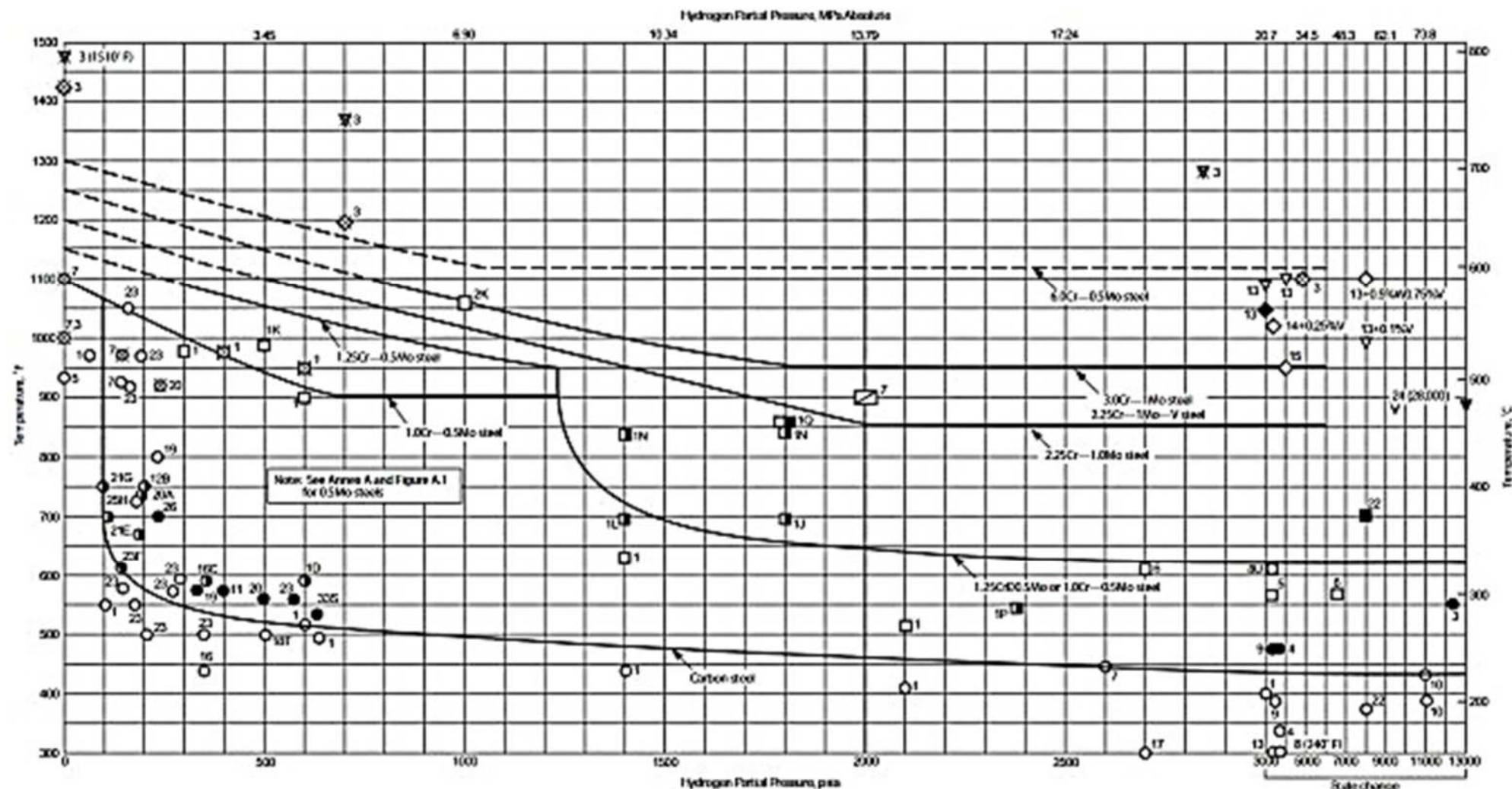


Figure 2. Microstructures observed after cooling to room temperature, and Continuous Cooling Transformation diagram determined by dilatometry.



Microstructures in a eutectoid steel. (a) Pearlite formed at 720 °C, (b) bainite formed at 290 °C, (c) bainite formed at 180 °C, and (d) martensite. [from Functions of the alloying elements in steel, Bain, E. C., American Society for Metals, Metals Park, Ohio, USA, 1939.





Notes:

1. The limits described by these curves are based on service experience originally collected by G.A. Nelson and on additional information gathered by or made available to API.
2. Austenitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.
3. The limits described by these curves are based on experience with cast steel as well as annealed and normalized steels at stress levels defined by Section VIII, Division 1, of the ASME Code. See 5.2 and 5.3 in text for additional information.
4. Several failures of 3-1/4Cr-1Mo steel have been reported in the satisfactory region. See Annex B for details.
5. The inclusion of the 2.25Cr-1Mo class of steels is based on 10,000-hr laboratory tests where these alloys were at least equal to the 3Cr-1Mo steel. See Reference 22 listed in the bibliography.

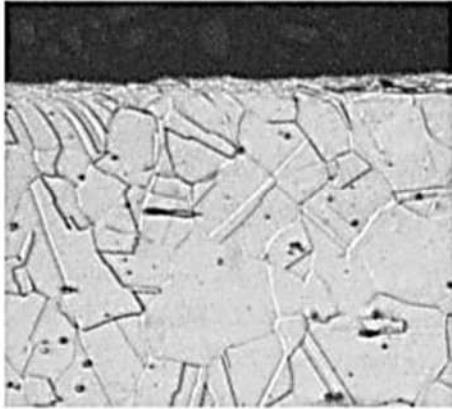
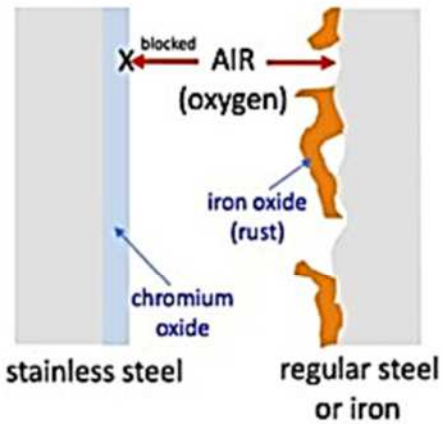
Copyright © 1961 by G.A. Nelson. Production rights granted by author to API.
This figure was revised by API in 1968, 1985, 1990 and 1996.

Legend:

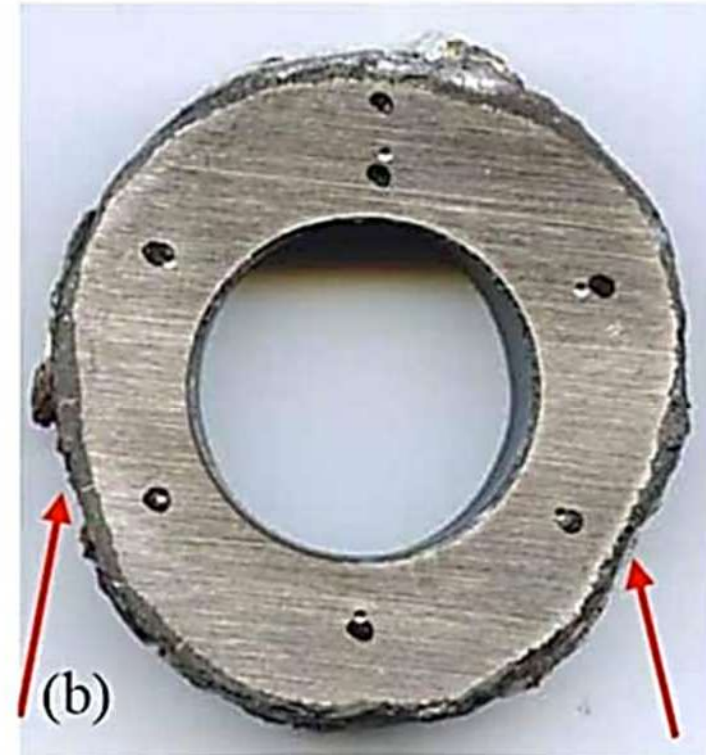
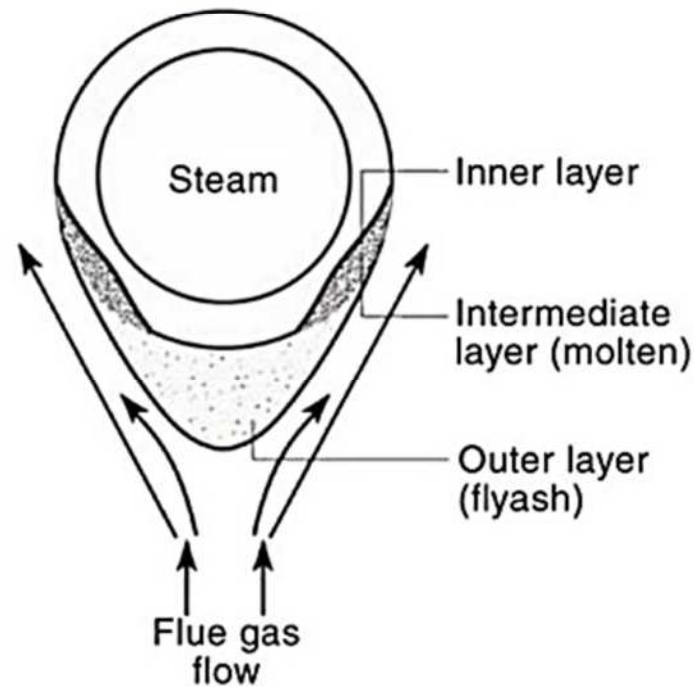
Surface decarburization	-----
Internal decarburization	-----
	Carbon steel 1.00Cr-0.5Mo 2.25Cr-1.0Mo 3.0Cr-1Mo 6.0Cr-0.5Mo
Satisfactory	○ □ ◇ ▼
Internal decarburization and fissuring	● ■ ◆ ▼
Surface decarburization	⊗ ⊗ ⊗ ⊗
See comments	⊙ ⊙ ⊙ ⊙

Figure 1—Operating Limits for Steels in Hydrogen Service to Avoid Decarburization and Fissuring

Chromium oxide blocks corrosion



Carburization of the tube surface, especially on austenitic alloys will decrease corrosion resistance and increase tube wastage rates. Corrosion rates under reducing conditions may be 2 to 5 times faster than under oxidizing conditions



4.4.5 Metal Dusting

4.4.5.1 Description of Damage

Metal dusting is form of carburization resulting in accelerated localized pitting which occurs in carburizing gases and/or process streams containing carbon and hydrogen. Pits usually form on the surface and may contain soot or graphite dust.

4.4.5.2 Affected Materials

Low alloy steels, 300 Series SS, nickel base alloys and heat resisting alloys. There is currently no known metal alloy that is immune to metal dusting under all conditions.

4.4.5.3 Critical Factors

- a) Process stream composition, operating temperature and alloy composition are critical factors.
- b) Metal dusting is preceded by carburization and is characterized by rapid metal wastage.
- c) Metal dusting involves a complex series of reactions involving a reducing gas such as hydrogen, methane, propane or CO.
- d) It usually occurs in the operating temperature range of 900°F to 1500°F (482°C to 816°C). Damage increases with increasing temperature.

e) The mechanism of metal dusting is considered to be:

1. Saturation of the metal matrix by carburization;
2. Precipitation of metal carbides at the metal surface and grain boundaries;
3. Deposition of graphite from the atmosphere onto the metal carbides at the surface;
4. Decomposition of the metal carbides under the graphite and metal particles; and
5. Further deposition of graphite catalyzed by the metal particles on the surface.

f) In high nickel alloys, it is thought that metal dusting occurs without the formation of metal carbides.

g) Metal dusting can also occur under alternating reducing and oxidizing conditions.

4.4.5.4 Affected Units or Equipment

a) Primarily fired heater tubes, thermowells and furnace components operating in carburizing environments are affected.

b) Metal dusting has been reported in catalytic reforming unit heater tubes, coker heaters, gas turbines, methanol reforming unit outlet piping and thermal hydro-dealkylation furnaces and reactors.

4.4.5.5 Appearance or Morphology of Damage

- a) In low alloy steels, the wastage can be uniform but usually is in the form of small pits filled with a crumbly residue of metal oxides and carbides.
- b) The corrosion product is a voluminous carbon dust containing metal particles and sometimes metal oxides and carbides. Frequently, this dust will be swept away by the flowing process stream, leaving behind only the thinned or pitted metal.
- c) In stainless and high alloy steels, the attack is frequently local, appearing as deep, round pits (Figure 4-125).
- d) Metallography will show that the metal is heavily carburized under the attacked surface (Figure 4-126).





Figure 4-125 – Metal dusting of a 304H stainless steel pipe.

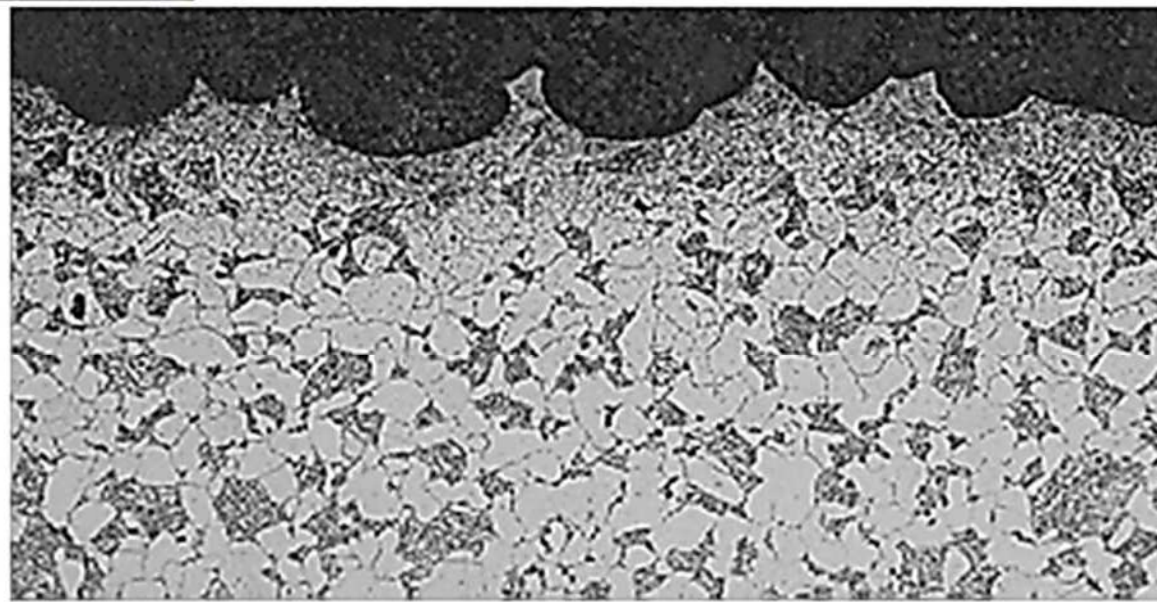


Figure 4-126 – Carbon steel separator plate in a natural gas preheater showing classical pattern of carburization and pitting

4.4.5.6 Prevention / Mitigation

- a) Sulfur in the carburizing atmosphere (usually as H_2S), forms a protective sulfide that minimizes carburization and metal dusting. It is thought that sulfur retards the carbon transfer from the atmosphere to the metal and suppresses graphite nucleation and growth. For protection, sufficient H_2S must always be in the process environment. If the H_2S level drops too low, even for a short period of time, damage may occur. Sulfur is a catalyst poison in some processing units so that the introduction of H_2S into a process stream may not always be practical.
- b) There is currently no known metal alloy that is immune to metal dusting under all conditions. Materials selection must be made based on the specific application and environment.
- c) An aluminum diffusion treatment to the base metal substrate can be beneficial in some applications.

4.4.5.7 Inspection and Monitoring

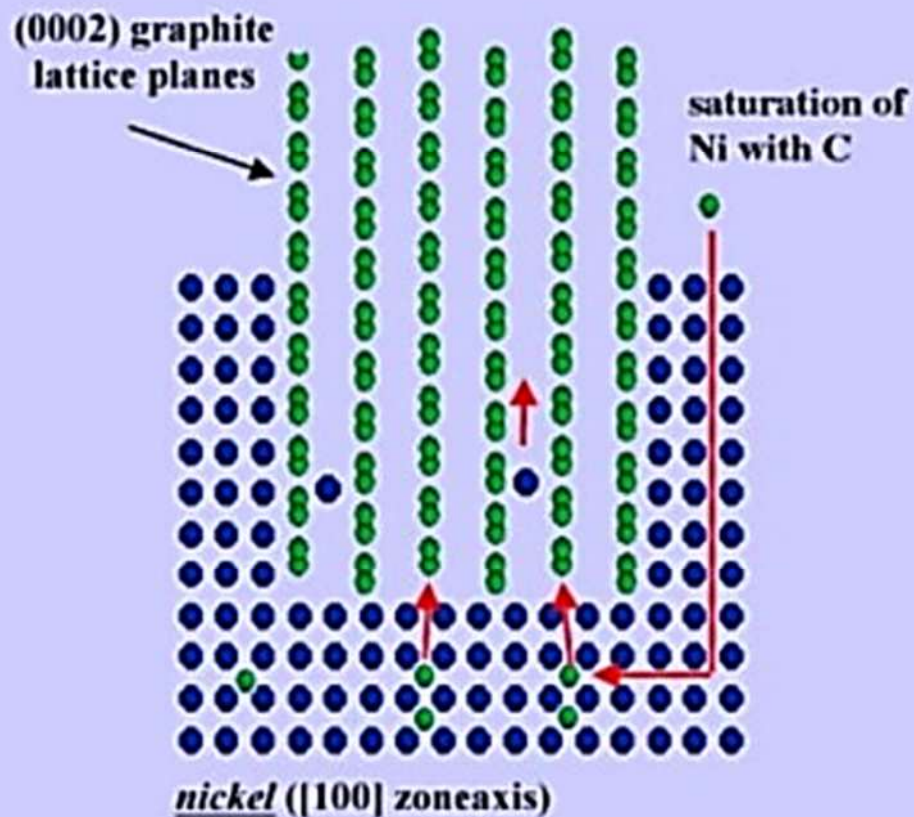
- a) For heater tubes with suspected damage, compression wave ultrasonic testing is probably the most efficient method of inspection since large areas can be inspected relatively quickly.
- b) RT techniques can be employed to look for pitting and wall thinning.
- c) If internal surfaces are accessible, visual inspection is effective.
- d) Filtering the cooled furnace or reactor effluent may yield metal particles that are a tell tale indication of a metal dusting problem upstream.

4.4.5.8 Related Mechanisms

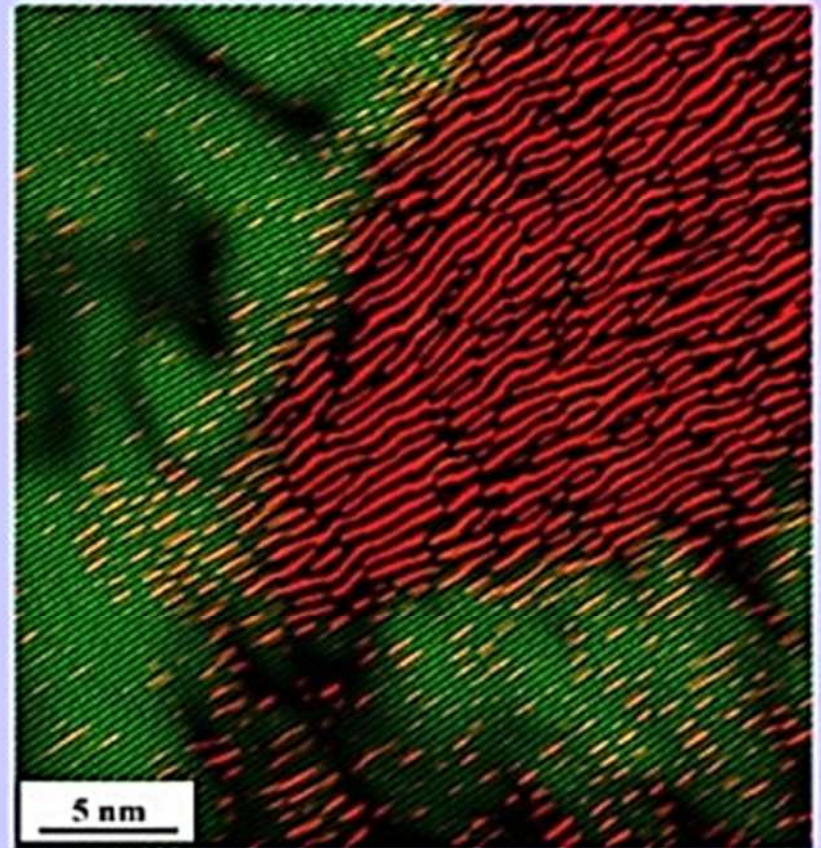
Metal dusting is also known as catastrophic carburization. Carburization is discussed in 4.4.3.

High temperature corrosion (metal dusting) of iron, steels and nickel alloys:

Atomic mechanisms of the disintegration of *nickel* by ingrowth of graphite basic planes with reactive ends



Scheme of the atomic processes



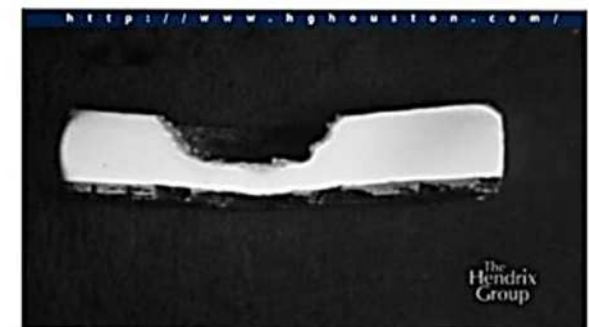
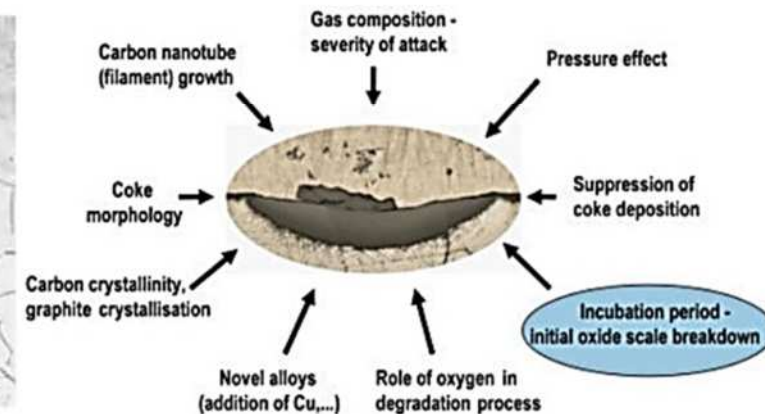
Numerically filtered (FFT) HREM image, showing the atomic planes of *carbon* (red) and the *metal* (green)



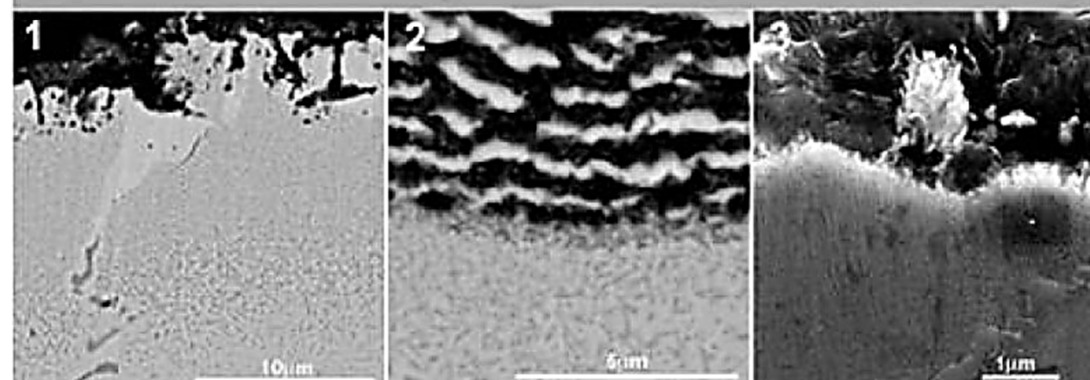
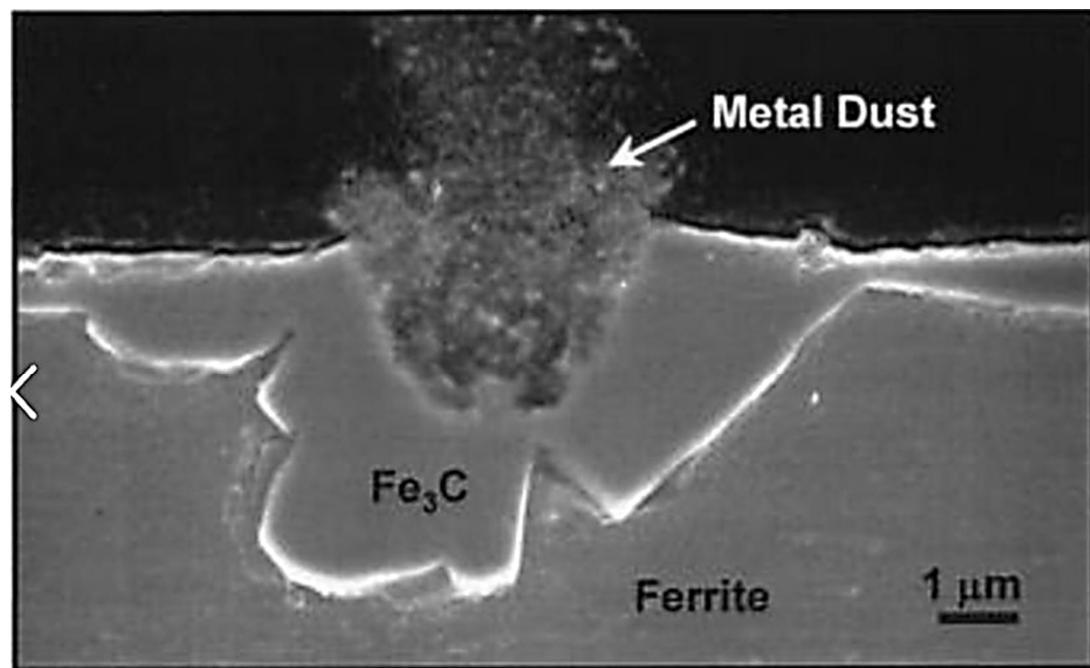
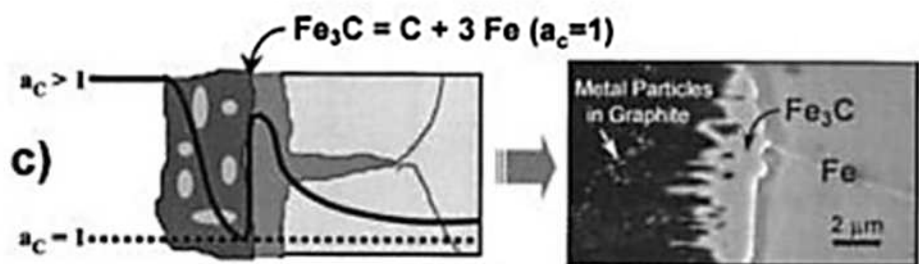
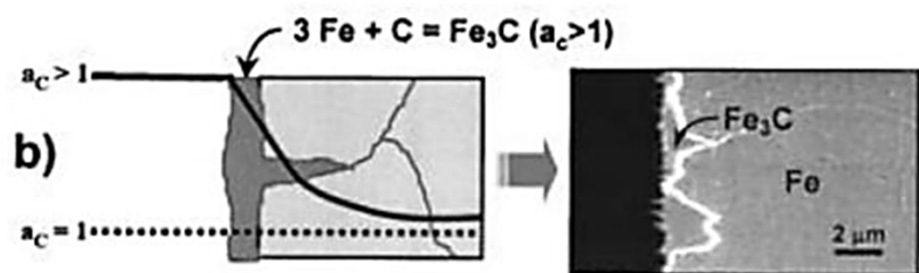
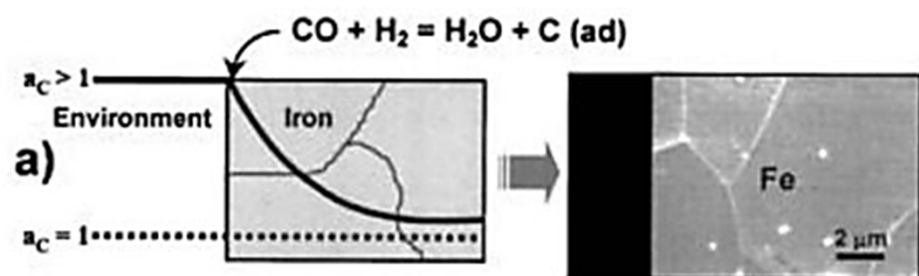
Metal dusting is form of carburization resulting in accelerated localized pitting which occurs in carburizing gases and/or process streams containing carbon and hydrogen. **Pits usually form on the surface and may contain soot or graphite dust.**

<http://mit.imt.si/Revija/fizvodi/mit026/grabke.pdf>

1- Close-up of pit shown in Photograph 10. The black material in the bottom of the pit is coke. The smaller pits (at arrows) are smaller versions of the large pit.



- Polished and etched cross-section through the I.D. pit. The thin gray band at the perimeter of the pit is an area of carburization. ~2.7X



http://www.mpi-halle.mpg.de/mpi/publi/pdf/2351_98.pdf

<http://www.diva-portal.org/smash/get/diva2:9563/FULLTEXT01.pdf>

4.4.6 Fuel Ash Corrosion

4.4.6.1 Description of Damage

- a) Fuel ash corrosion is accelerated high temperature wastage of materials that occurs when contaminants in the fuel form deposits and melt on the metal surfaces of fired heaters, boilers and gas turbines.
- b) Corrosion typically occurs with fuel oil or coal that is contaminated with a combination of sulfur, sodium, potassium and/or vanadium.
- c) The resulting molten salts (slags) dissolve the surface oxide and enhance the transport of oxygen to the surface to re-form the iron oxide at the expense of the tube wall or component.

4.4.6.2 Affected Materials

- 1. All conventional alloys used for process heater and boiler construction are susceptible.
- 2. Alloys of the 50Cr-50Ni family show improved resistance.

4.4.6.3 Critical Factors

- a) The concentration of molten salt forming contaminants, metal temperature and alloy composition are the critical factors.
- b) The severity of damage depends on the type of fuel (i.e., the concentrations of contaminants in the fuel), sulfur content and metal temperature.
- c) Corrosion occurs by this mechanism only if the metal temperature is above the temperature of the liquid species formed, and it is most severe where the temperatures are the highest.
- d) The corrosion rates differ depending on the alloy and location within the heater.

- e) The liquid species (slags) are different for the oil and coal ash and are also different for water walltube corrosion.
1. For oil ash, the liquid species are mixtures of vanadium pentoxide and sodium oxide, or vanadium pentoxide and sodium sulfate. Depending on the precise composition, melting points below 1000°F (538°C) are possible.
 2. For waterwall corrosion, the liquid species are mixtures of sodium and potassium pyrosulfates that have melting points as low as 700°F (371°C).
 3. For coal ash, superheater and reheater corrosion is caused by sodium and potassium iron trisulfates that melt between 1030°F and 1130°F (544°C and 610°C), depending on the ratio of sodium and potassium. Reducing conditions, that is, a flue gas rich in carbon monoxide, hydrogen sulfide and hydrogen will aggravate the corrosion rates.
- f. Unburned coal particles also add carbon to the fly ash deposits and provide a reducing environment on the tube surface where corrosion occurs. Carburization of the tube surface, especially on austenitic alloys will decrease corrosion resistance and increase tube wastage rates.
- g. Corrosion rates under reducing conditions may be 2 to 5 times faster than under oxidizing conditions.

4.4.6.4 Affected Units or Equipment

- a) Fuel ash corrosion can occur in any fired heater or gas turbine utilizing fuels with the aforementioned contaminants.
- b) Fuel ash corrosion is most often associated with fired heaters burning vanadium and sodium contaminated fuel oils or residue.
- c) Heater tubes are sometimes not affected because their skin temperatures are cooler than the threshold melting point of the slags in most heaters. Tube hangers and supports, however, operate hotter and can suffer severe fuel ash corrosion.
- d) Some gas turbines suffer blade corrosion when switched over to burning fuel oil.
- e) In some cases, coking of the heater tubes may cause operators to increase heat flux that may push some components above the threshold temperature where fuel ash corrosion is possible.
- f) Since the melting points of these liquid species are around 1000°F (538°C) and higher in the superheaters and reheaters, any unit that has metal temperatures above the melting point of the sulfates may have the problem.
- g) For oil-fired boilers, fuel oils that do not contain vanadium are less prone to liquid ash corrosion.
- h) For waterwalls, if the temperature can be maintained below the melting point of the pyrosulfates [that is below 700°F (371°C)], damage will be minimized. Thus, steam generating pressures below about 1800 psi are nearly immune.

4.4.6.5 Appearance or Morphology of Damage

- a) Oil ash corrosion is manifested as severe metal loss associated with slagging. In some cases, corrosion rates of 100 to 1000 mpy may be experienced.
- b) Metallographic examination and deposit-analysis techniques can be used to verify the presence of fuel ash corrosion.
- c) For oil ash corrosion of superheaters and reheaters, the appearance of the ash deposit will be in at least two distinct layers. The important deposit is adjacent to the component, which will have a dark gray or black appearance at room temperature. As the liquid sulfates sinter the corrosion debris to the surface, a hard, glassy, tenacious scale is formed. When removed, the surface of the steel will have an "alligator-hide" appearance (Figure 4-127 and Figure 4-128) as shallow grooves will have penetrated the steel in a cross-hatched pattern.
- d) For waterwalls, the cracks are predominantly circumferential and, to a lesser extent, axial. The overall appearance on the waterwalls is one of circumferential grooving.
 - 1. After the liquid ash layer develops, the "slush" can only hold a certain weight of ash. When the weight is excessive, the slag is shed, exposing a bare, uninsulated tube to the heat flux of the firebox. The temperatures will spike on waterwalls, by perhaps 100°F (38°C) and the cracking is then similar to thermal fatigue.
 - 2. The mechanism for the steam-cooled tubes is similar, except that the temperature spike is probably less and, therefore, the thermal fatigue damage is less severe.
 - 3. The alligator-hide morphology of superheaters and reheaters and the circumferential cracking on waterwalls in coal-fired boilers is caused by a similar mechanism.
- e) For coal ash, the appearance will be a smooth interface between a glassy slag layer and the metal.

4.4.6.6 Prevention / Mitigation

- a) Fuel ash corrosion can be prevented by blending or changing fuel sources (minimizing the contaminants) and by operating equipment so that hot components are below the temperature where molten deposits are formed.
- b) Proper burner design and burner management can help to reduce flame impingement and localized hot spots.
- c) In some cases, the characteristics and melting points of the slags can be changed by firing **with low excess oxygen** or by injecting special additives into the fuel. These changes can increase the melting point of the slags and reduce the tendency of the deposits to stick to metal surfaces or dissolve the protective oxide scale. Even with changes to reduce slag formation, corrosion may continue if metal surfaces are not cleaned to remove slag and corrosion products.
- d) Corrosion of some components, such as tube hangers and supports, can be minimized by changing to a 50%Cr-50%Ni alloy, such as Alloy 657. Designs of tube hangers may need to be modified to account for the lower stress-rupture strength of the 50Cr-50Ni alloys.

4.4.6.7 Inspection and Monitoring

- a) Visual inspection is usually sufficient to detect hot ash corrosion.
- b) Metal loss is likely to be severe and the presence of a slag will be apparent.
- c) Tubes need to be grit blasted in order to remove the tenacious glass-like ash deposit. UT examination may be useful to measure loss of thickness.

4.4.6.8 Related Mechanisms

- a) Hot corrosion, hot ash corrosion, molten salt corrosion, oil ash corrosion and coal ash corrosion are all terms used to describe this mechanism.
- b) Circumferential cracking in waterwall tubes is similar to thermal fatigue aggravated by a corrosive environment (Figure 4-129).



Figure 4-127 – The “alligator hide” morphology of liquid coal-ash corrosion is evident when the dense, glassy deposit is removed. Mag. 2.4X

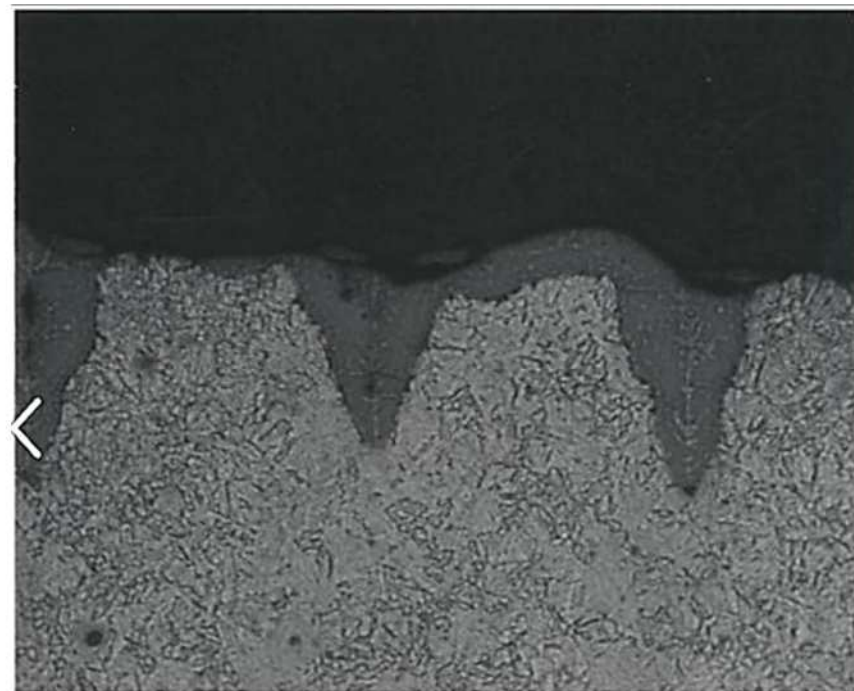


Figure 4-128 – In cross-section, the surface grooving is, in actuality, broad, V-shaped corrosion fatigue cracks. Mag. 100X, etched.

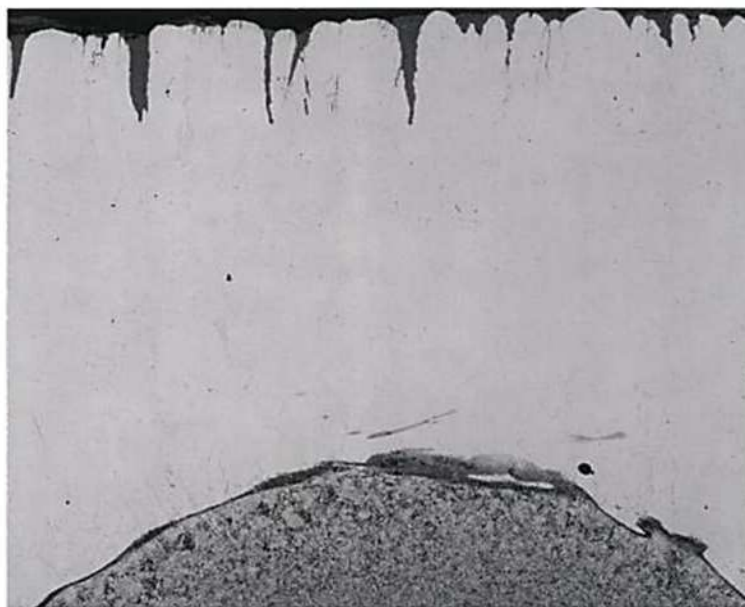
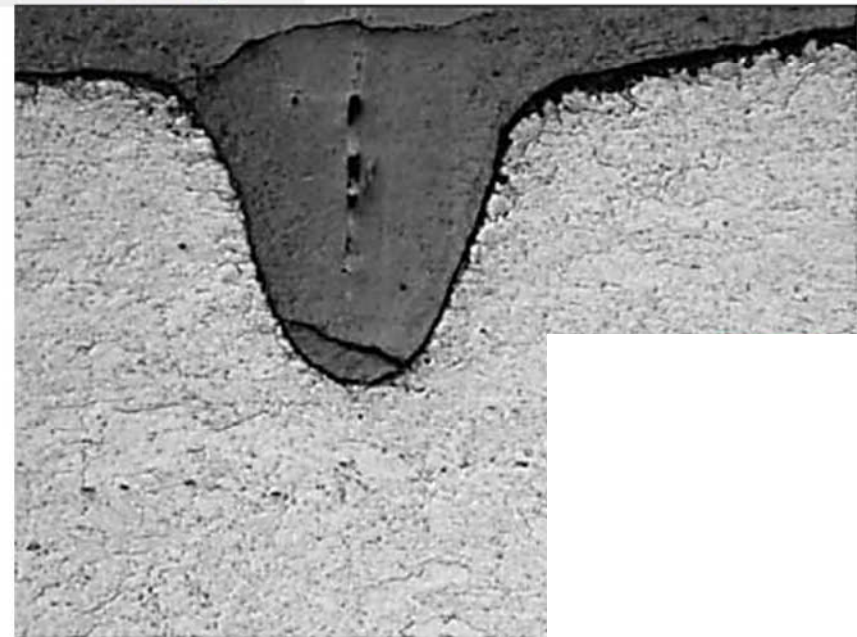
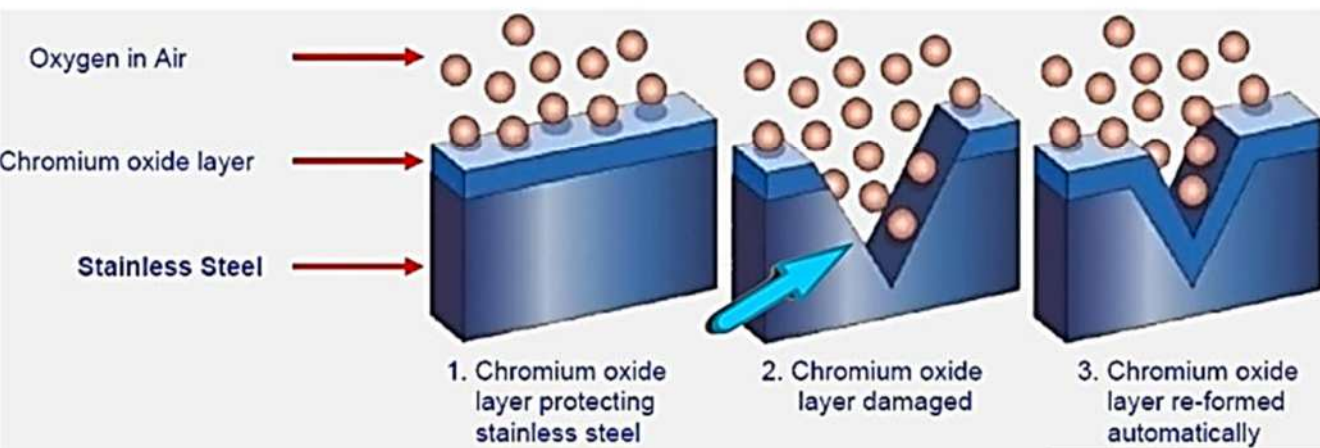


Figure 4-129 – On waterwall tubes, even with a corrosion-resistant weld-overly, circumferential cracking will develop. Mag. 37½X, etched.

Molten salts (slags) dissolve the surface oxide and enhance the transport of oxygen to the surface to re-form the iron oxide at the expense of the tube wall or component.



The Role of Fireside Corrosion on Boiler Tube Failures, Part I

<http://www.maintenanceworld.com/the-role-of-fireside-corrosion-on-boiler-tube-failures-part-1/>

<http://www.powermag.com/the-role-of-fireside-corrosion-on-boiler-tube-failures-part-2/>

4.4.7 Nitriding

4.4.7.1 Description of Damage

A hard, brittle surface layer will develop on some alloys due to exposure to high temperature process streams containing high levels of nitrogen compounds such as ammonia or cyanides, particularly under reducing conditions.

4.4.7.2 Affected Materials

Carbon steels, low alloy steels, 300 Series SS and 400 Series SS.
Nickel base alloys are more resistant.

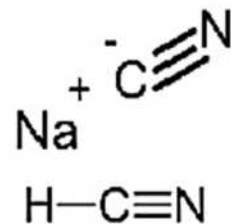
4.4.7.3 Critical Factors

- a) Nitriding is a diffusion controlled process dependent on temperature, time, partial pressure of nitrogen and metal composition.
- b) Temperatures must be high enough to allow for the thermal breakdown/disassociation of nitrogen from ammonia or other compounds and for diffusion of nitrogen into the metal.
- c) Nitriding begins above 600°F (316°C) and becomes severe above 900°F (482°C).
- d) High gas phase nitrogen activity (high partial pressures of nitrogen) promotes nitriding.
- e) Corrosion resistance may be adversely affected by nitriding.
- f) Alloys containing 30% to 80% nickel are more resistant.
- g) A loss of high temperature creep strength, ambient temperature mechanical properties (specifically toughness/ductility), weldability and corrosion resistance may result.

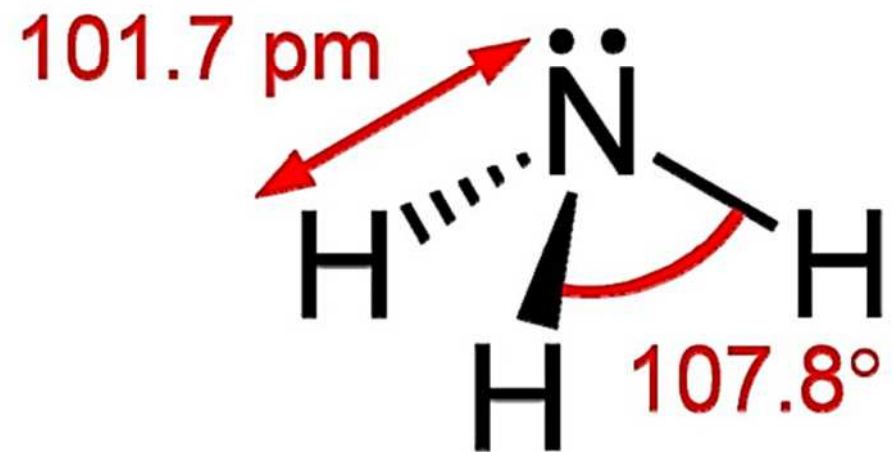
4.4.7.4 Affected Units or Equipment

Nitriding can occur at any location where appropriate environment and temperature conditions are met, but it is considered to be fairly rare. Nitriding has been observed in steam methane-reformers, steam gas cracking (olefin plants) and ammonia synthesis plants.

Cyanide hydrogen cyanide
Sodium cyanide



Ammonia



4.4.7.5 Appearance or Morphology of Damage

- a) Nitriding is usually confined to the surface of most components and will have a dull, dark gray appearance. However, during initial stages of nitriding, damage can only be seen with metallography as shown in Figure 4-130, Figure 4-131 and Figure 4-132.
- b) In a more advanced stage, the material will exhibit very high surface hardness. In most cases, a slightly harder surface layer of a vessel or component will not affect the mechanical integrity of the equipment. However, the concern is for the potential development of cracks in the nitrided layer that could propagate into the base metal.
- c) Nitriding of low alloy steels containing up to 12% chromium is accompanied by an increase in volume. The nitrided layer tends to crack and flake.
- d) Above 770° F (410° C), preferential grain boundary nitriding may lead to microcracking and embrittlement.
- e) Stainless steels tend to form thin, brittle layers that may crack and spall from thermal cycling or applied stress.
- f) Nitrogen diffuses into the surface and forms needle-like particles of iron nitrides (Fe_3N or Fe_4N) that can only be confirmed by metallography.

4.4.7.6 Prevention / Mitigation

Changing to more resistant alloys with 30% to 80% nickel is usually required. It is usually not practical to modify the process conditions to reduce the nitrogen partial pressure or to lower temperatures.



Figure 4-130 – A nitrided 5Cr-0.5Mo thermowell from an ammonia synthesis plant with surface cracking.

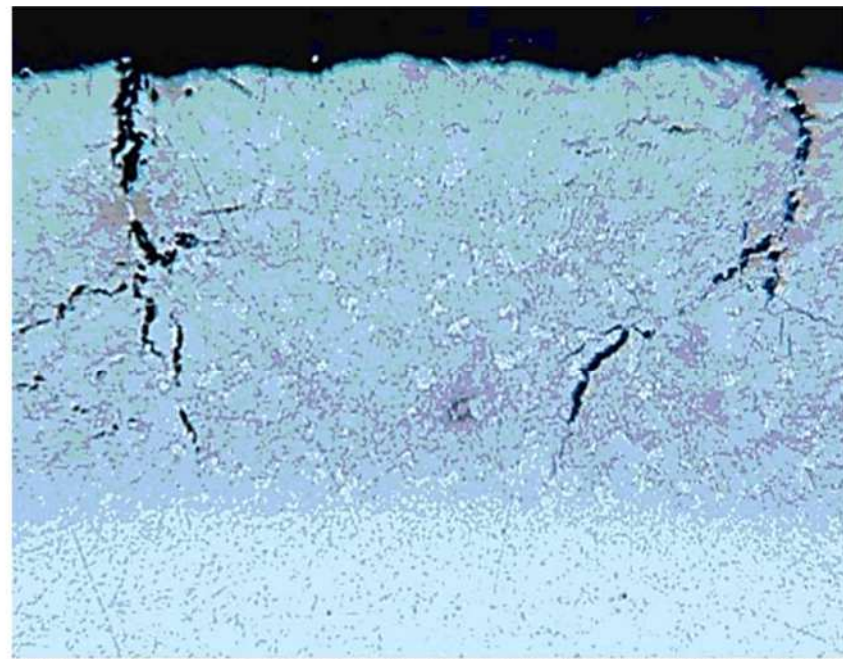


Figure 4-131 – A photomicrograph of a cross-section through the tube showing the interface between the shallow nitrided layer on the surface (gray) and the unaffected base metal (white). Cracks initiate from the O.D. surface at the top. Mag. 50X.

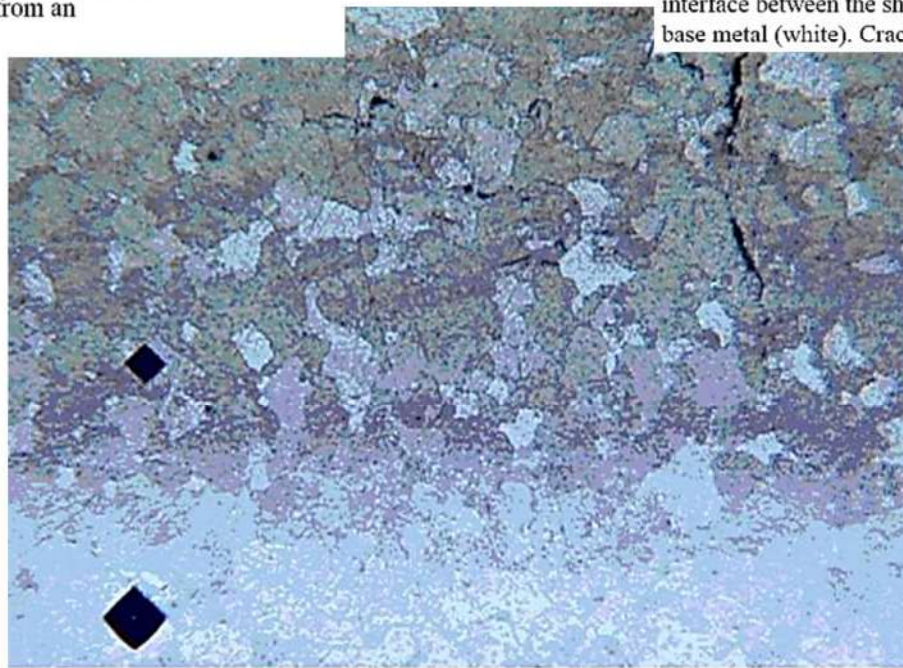


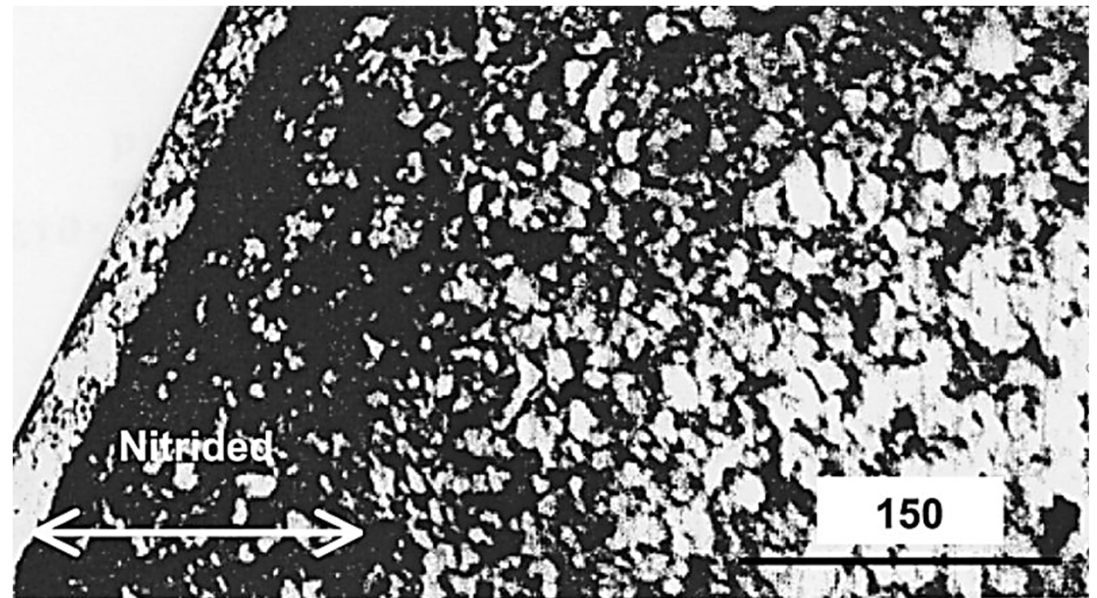
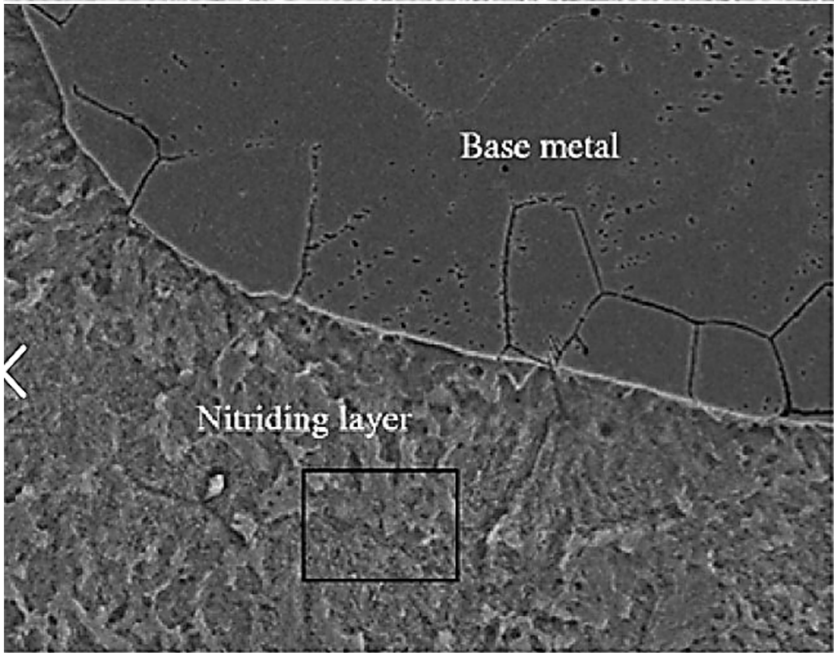
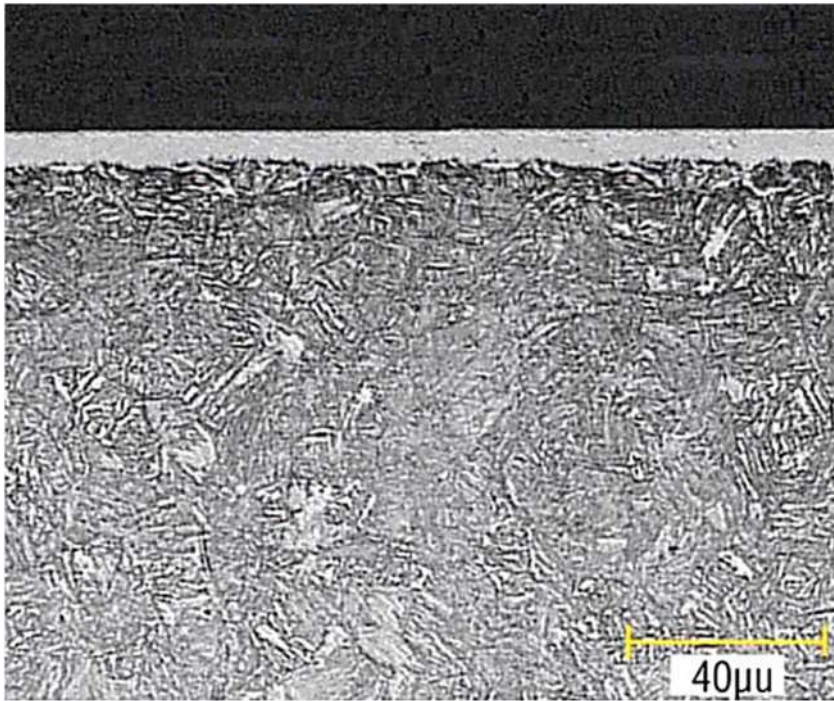
Figure 4-132 – A higher magnification photomicrograph showing the diamond-shaped hardness indentations in the hard nitrided layer (540 BHN) versus the softer base metal (210 BHN). Mag. 150X.

4.4.7.7 Inspection and Monitoring

- a) A change in surface color to a dull gray may indicate nitriding.
- b) Materials exposed to nitriding conditions should be inspected thoroughly because good appearance may mask damage.
- c) Hardness testing of the affected surfaces (400 to 500 BHN or higher) can help indicate nitriding.
- d) Nitrided layers are magnetic. Therefore, 300 Series SS should be checked for magnetism as an initial screening.
- e) Metallography is generally required to confirm nitriding.
- f) EC testing may be used in some cases to detect nitriding.
- g) In the advanced stages of nitriding, where cracking may have initiated, appropriate inspection techniques include PT, RT and UT.

4.4.7.8 Related Mechanisms

Similar gas-metal surface reactions occur in other environments including carburization (see 4.4.3) and metal dusting (see 4.4.5).



60 µm Electron image 1