Inspection Department

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High Temperature Corrosion

As per API 571, Corrosion which occurs above 204°C, consider as high temp corrosion

1. Oxidation
2. Carburization
3. Metal Dusting
4. Sulfidation
5. Nitriding

Oxidation

Oxidation

Highlights:

1. Oxygen reacts with carbon steel and other alloys at high temperature converting the metal to oxide scale.

2. Affected metals: All iron based materials including carbon steel and low alloy steels, All 300 Series SS, 400 Series SS and nickel base alloys also oxidize to varying degrees, depending on composition and temperature.

3. The primary factors affecting high temperature oxidation are metal temperature and alloy composition.

4. Oxidation of carbon steel begins to become significant above about 1000°F (538°C). Rates of metal loss increase with increasing temperature.

Highlights:

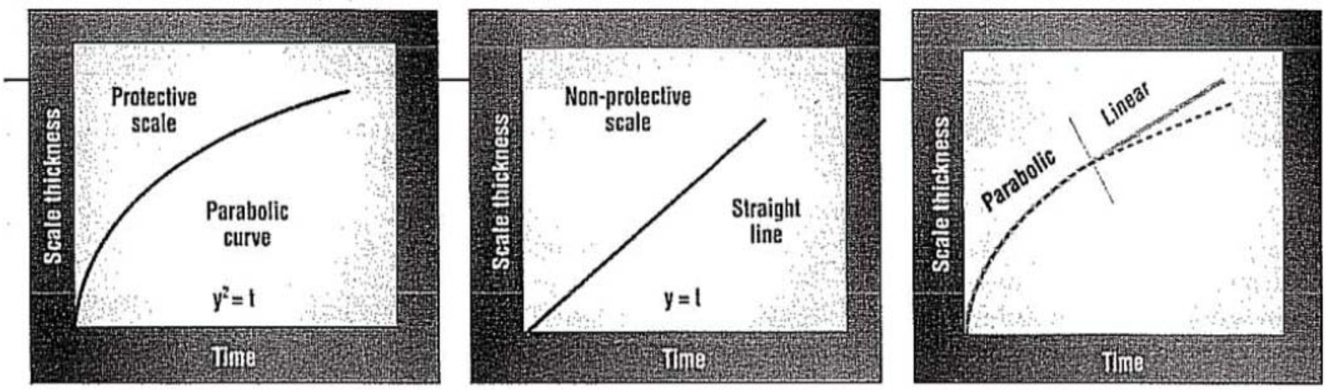
5. In general, the resistance of carbon steel and other alloys is determined by the chromium content of the material. Increasing chromium levels produce a more protective oxide scale. The 300 Series SS are resistant to scaling up to about 1500°F (816°C).

6. The presence of water vapor can significantly accelerate oxidation rates of some steels.

7. 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.

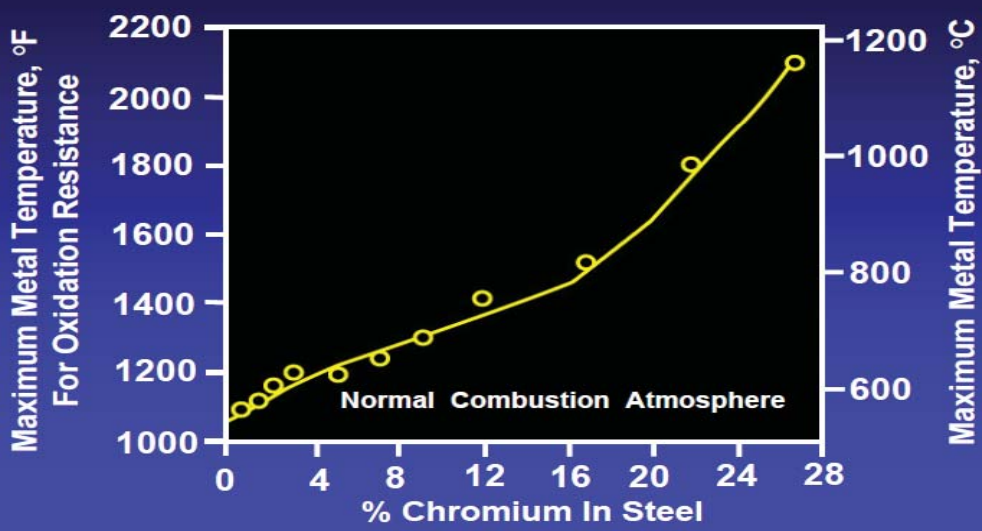
8. Chromium is the primary alloying element that affects resistance to oxidation. Other alloying elements, including silicon and aluminum, are effective but their oncentrations are limited due to adverse affects on mechanical properties. They are often used in special alloys for applications such as heater supports, burner tips and components for combustion equipment.

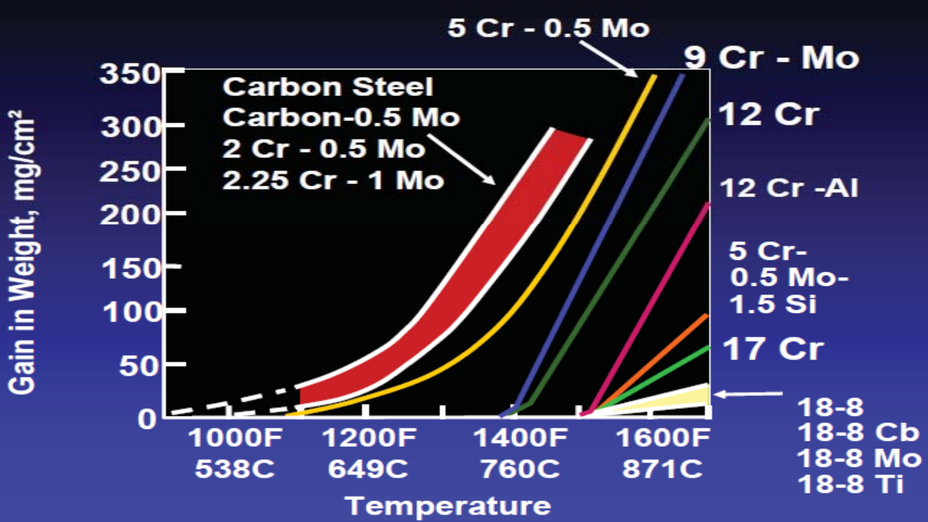
Oxidation



Material	Maximum Metal Temperature (°C)											
	496	524	552	579	607	635	663	691	718	746	774	802
CS	0.05	0.1	0.15	0.23	0.36	0.56	0.84	1.22	--	--	--	--
1 1/4 Cr	0.05	0.08	0.1	0.18	0.3	0.46	0.76	1.17	--	--	--	--
2 1/4 Cr	0.03	0.03	0.05	0.1	0.23	0.36	0.61	1.04	--	--	--	--
5 Cr	0.03	0.03	0.03	0.05	0.1	0.15	0.38	0.89	1.65	--	--	--
7 Cr	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.15	0.43	0.94	1.52	--
9 Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.13	0.28	0.58	1.02
12 Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.08	0.2	0.38	0.76
304 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.1
309 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08
310 SS / HK	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
800 H / HP	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05

Effect Of Chromium On Oxidation Resistance of Steel





Amount of oxidation (scaling) of carbon, low-alloy, and stainless steels in 1000 hours in air from 1000° to 1700°F (538° to 926°C)

Carburization

Carburization

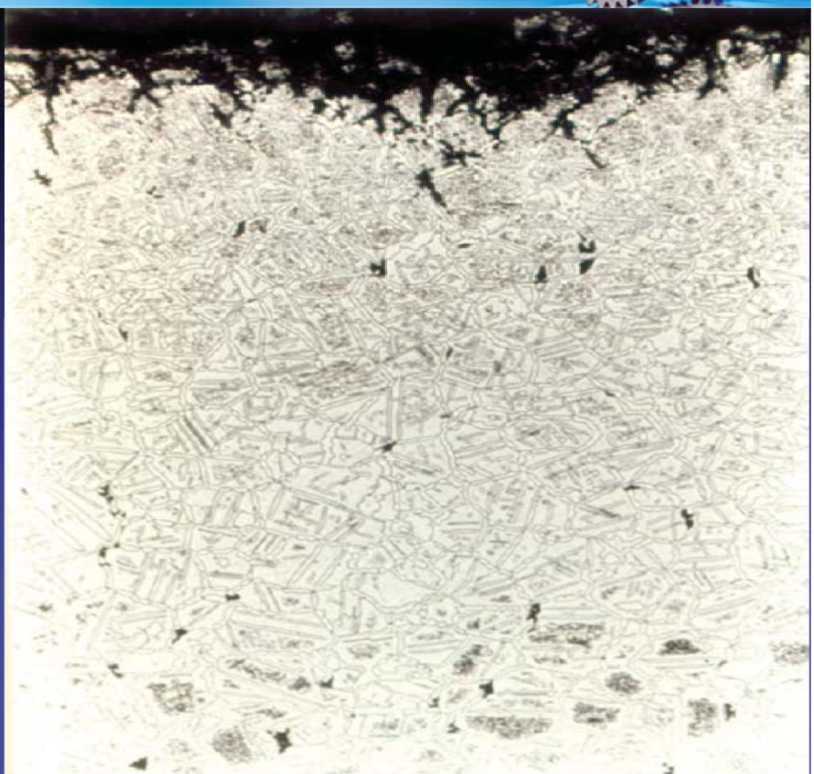
Highlights:

1. Carburization occurs when metals are exposed to carbon monoxide, methane or any hydrocarbon at elevated temp.
2. During process, carbon combines primarily with chromium and forms carbide, this process is called carbon uptake.
3. Since these carbides are brittle, they can reduce the alloy overall ductility especially at temp below 550 deg cel.
4. Carbide formation causes metal to increase its volume.
5. The stress of localized bulging in tubes reduces the creep strength and contributes to mechanical failure.
6. By tying up with chromium, carburization also reduces the metal resistance to high temp. to oxidation.

- Occurs in CH_4, CO and other hydrocarbon environments at elevated temperatures
- It is highly embrittling
- Grain boundary and internal carbides form
- Reduction or prevention:
  - Smooth surface finish
  - Inject low levels of S compounds into the process stream (to poison the carburizing reaction)
  - Modify the composition:
    - Increased Ni: reduces C diffusion
    - Increased Si: forms SiO_2 scale
    - High levels (4%) of Al
    - Minor element additions – Ti, Nb, W, Mo, rare earths

Austenitic stainless steel exposed to carburizing conditions

Carbon combines with chromium to form chromium carbides leaving behind Ni and Fe, both of which are magnetic



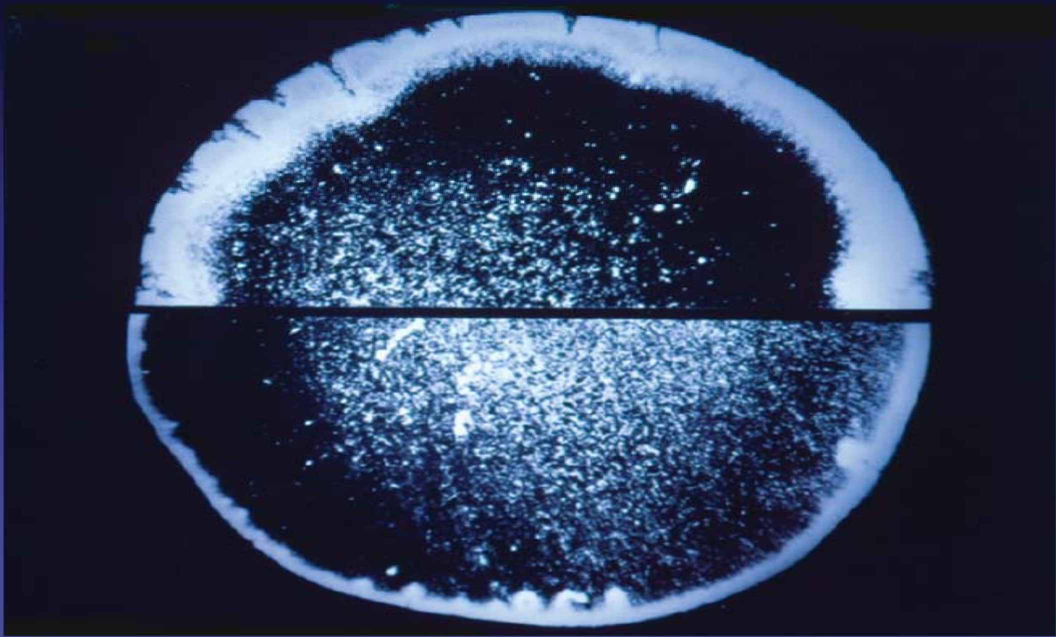
Two alloys exposed to the same carburizing conditions

Top:

Alloy 601 (61% Ni)

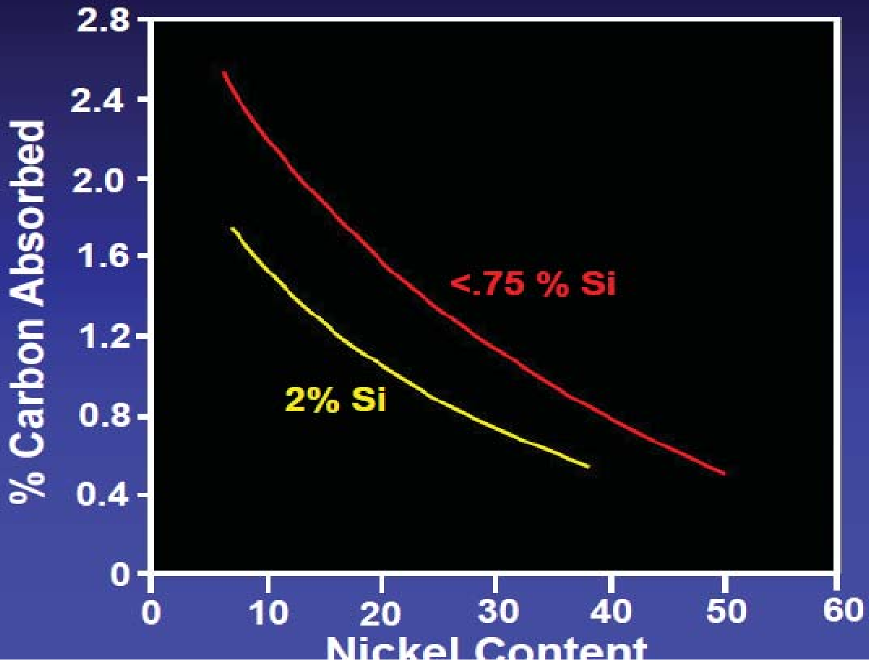
Bottom:

Alloy 600 (76% Ni)



Effect of Si and Ni On Carburization Resistance

1832°F (1000°C) For 200 Hours in Carbon Granulate



Cast HP-Mod ethylene furnace tubes after magnetic particle inspection – the dark areas are carburized

Note the variability:

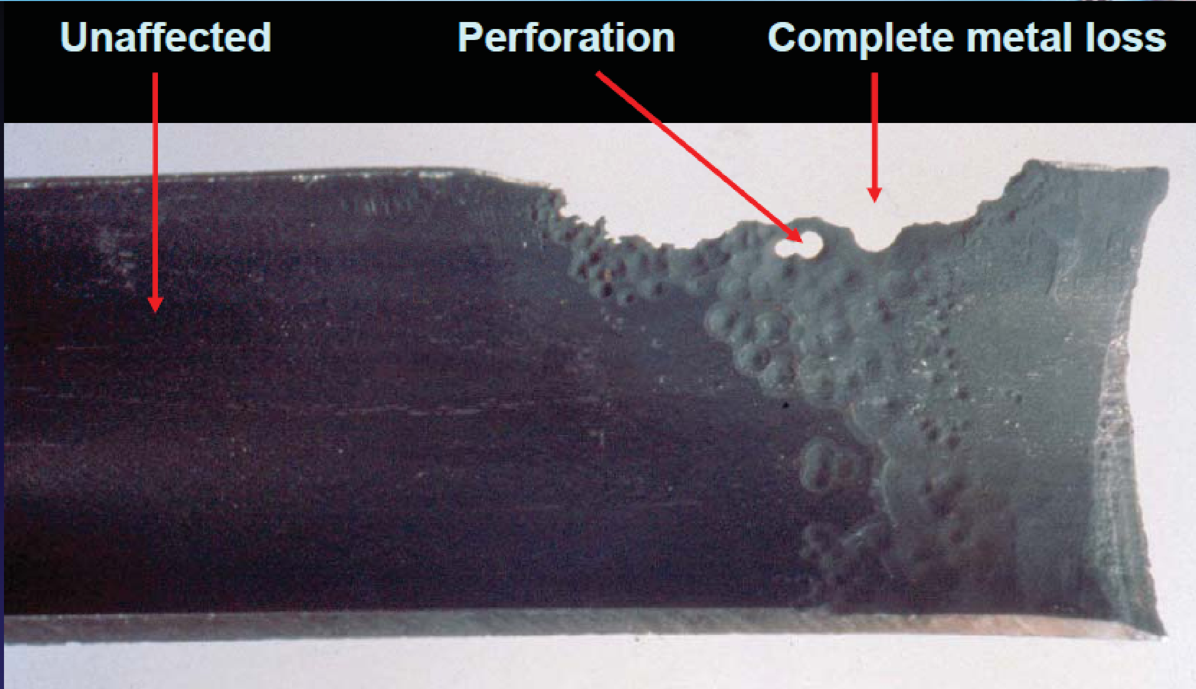
some sections are heavily carburized

other nearby sections are largely unaffected

Metal Dusting

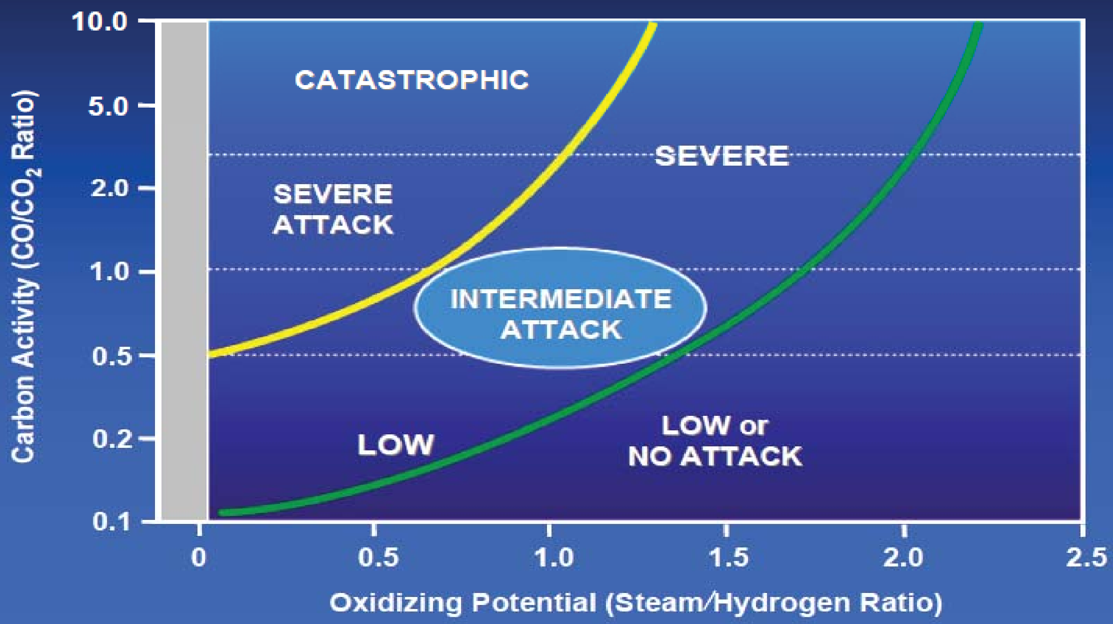
It is a catastrophic carburization phenomenon which occurs when the carbon activity in the gaseous atmosphere is greater than1

- Catastrophic carburization – very rapid
- Occurs in CO, CO_2, and H environments at 900-1650°F (480-900°C)
- Stagnant areas are more prone to attack
- Round bottom pits
- Surface of remaining area is heavily carburized
- Most alloys are attacked
- Unpredictable
- Steam and S additives are sometimes effective controllers

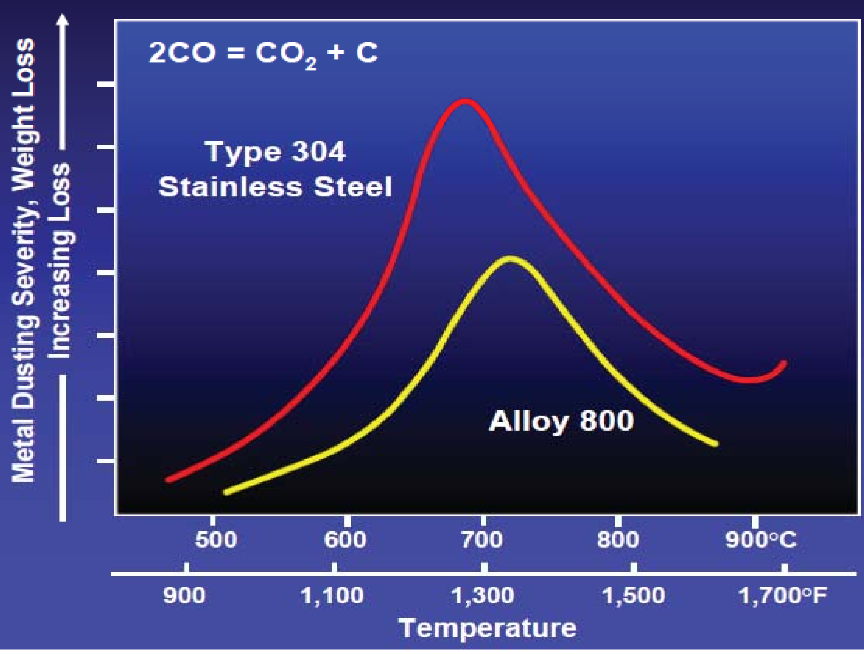


HP-Mod cast ethylene furnace tube showing metal dusting
Note its localised nature

EFFECT OF CO/CO_2 RATIO ON METAL DUSTING IN CRITICAL TEMPERATURE RANGE VERSUS STEAM/HYDROGEN RATIO (AS APPLICABLE TO STAINLESS 304 AND ALLOY 800)



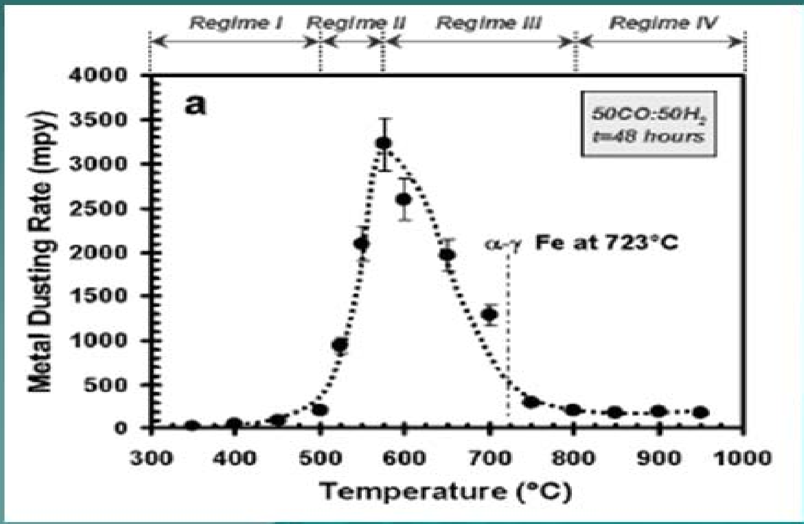
METAL DUSTING CAN RESULT IN SEVERE ATTACK IN CERTAIN TEMPERATURES



METAL DUSTING RATE

VS TEMPERATURE

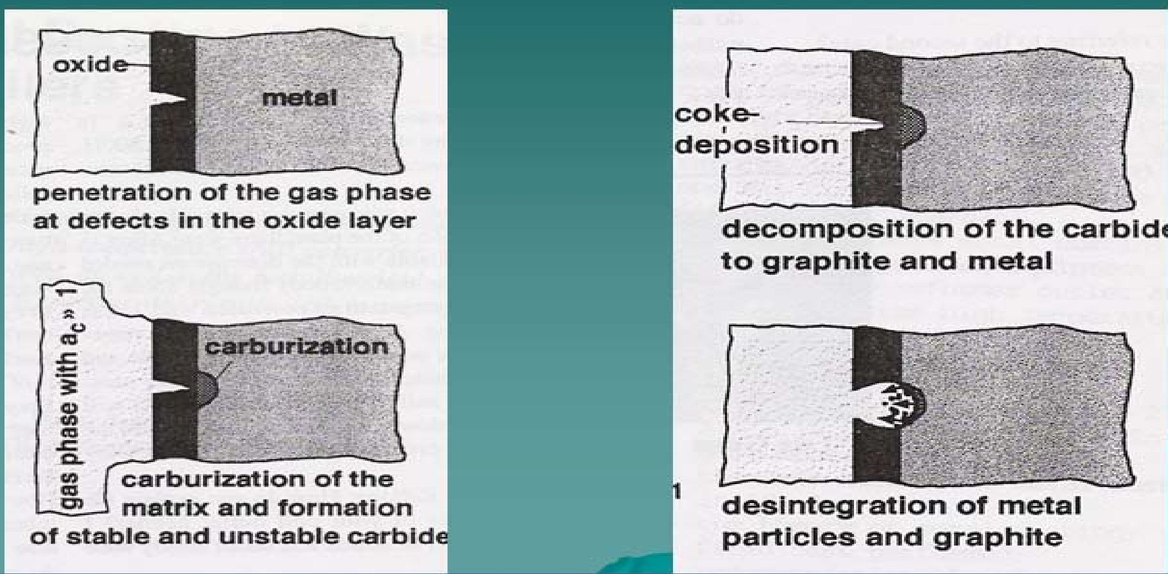
In regime I the corrosion rate gradually increases with temperature,
In regime II the corrosion rate undergoes a rapid rise,
In regime III the corrosion rate decreases with temperature and
In regime IV, the rate is more or less constant.



MECHANISM OF METAL DUSTING

CARBON DEPOSITION BY BOUDOURD REACTION :

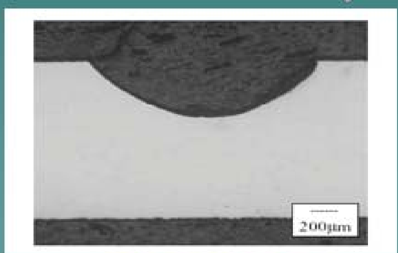
$2CO = CO_2 + C$



Metal Dusting Control – Process Modification

- Adding sulphur to the RG or reducing the CO/CO_2 ratio by adding extra CO_2 in the feed to the primary reformer. Both these are not feasible because the sulphur is poison for the catalyst and no additional CO_2 is available in the urea base fertilizer plant.
- Because of extra CO2 availability this has been used in Methanol plant

CONDITION OF SPECIMEN AFTER TEST



ALLOY 6600
After 6600 Hrs

ALLOY 693
After 15816 Hrs.

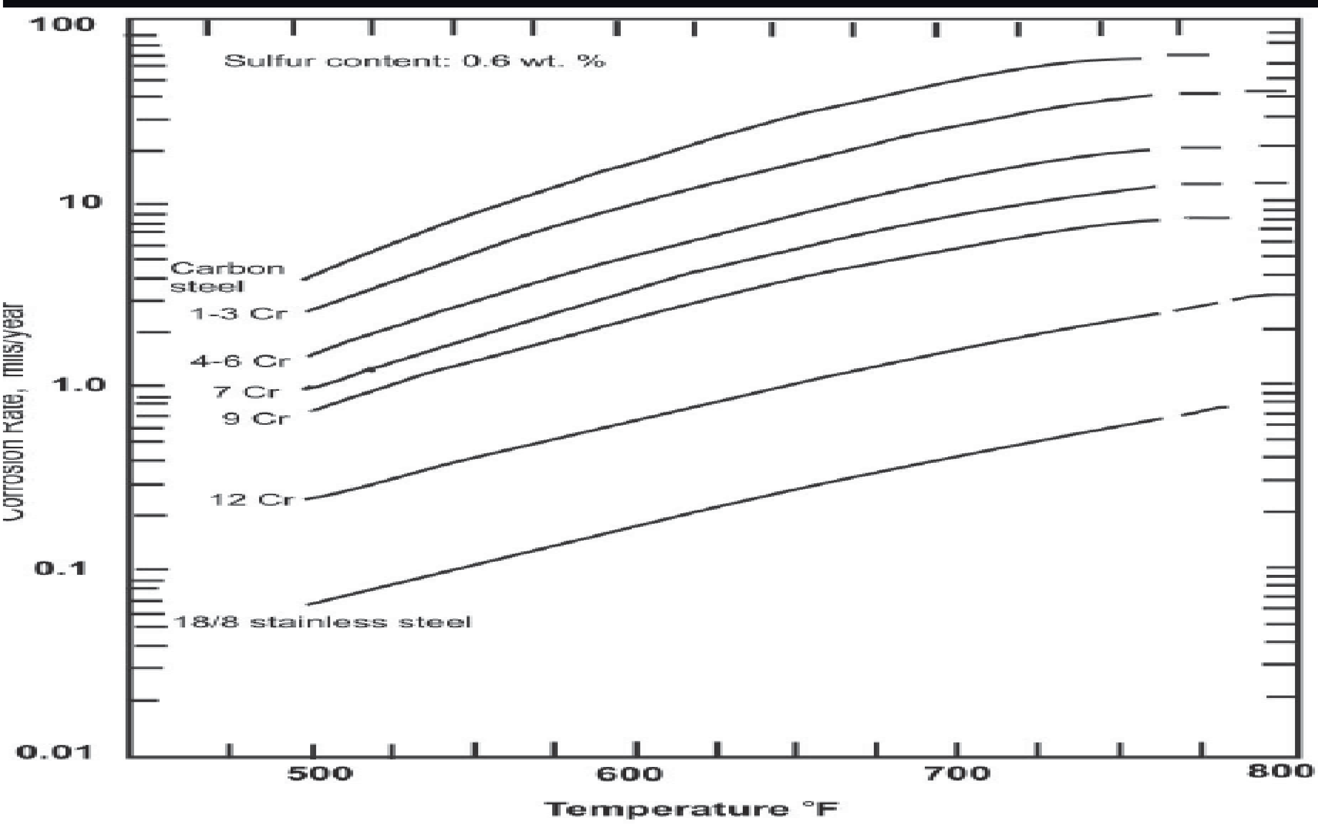
CHROMIUM EQUIVALENTS
VARIOUS WROUGHT AND CAST ALLOYS
Cr eq = Cr% + 3 x (Si% + Al%)

UNS Number	Alloy	Composition (wt %)					Metal Dusting Resistance
		Cr	Ni	Si	Al	Cr eq	
Wrought alloys							
N08810	800H	20	32	.3	.3	22	poor
S31000	310SS	25	20	.3	-	26	fair
N06600	Inc. 600	15	72	-	-	15	fair
N06601	Inc. 601	22	60	-	1.5	27	good
	Kanthal APM	22	-	-	6.0	40	best
Cast alloys							
J94204	HK-40	25	20	1.0	-	28	good
N08705*	HP-mod	26	35	1.5	-	30	good
	Manoir XTM	35	48	1.5	-	40	best

Sulfidation

Highlights:

1. Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high temp. environment
2. Susceptibility of an alloy to sulfidation is determined by its ability to form protective sulfide scales.
3. Sulfidation of iron-based alloys usually begins at metal temperatures above 500°F (260°C).
4. Heaters fired with oil, gas, coke and most other sources of fuel may be affected depending on sulfur levels in the fuel.
5. 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



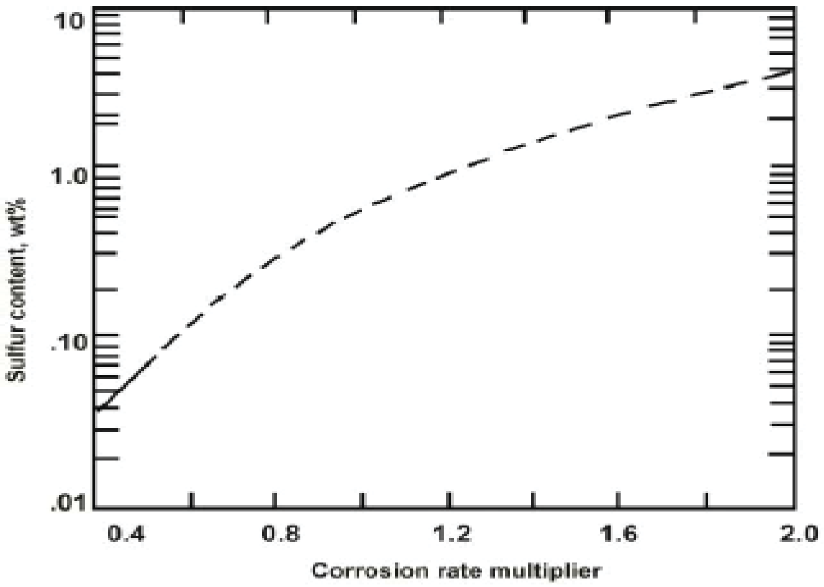
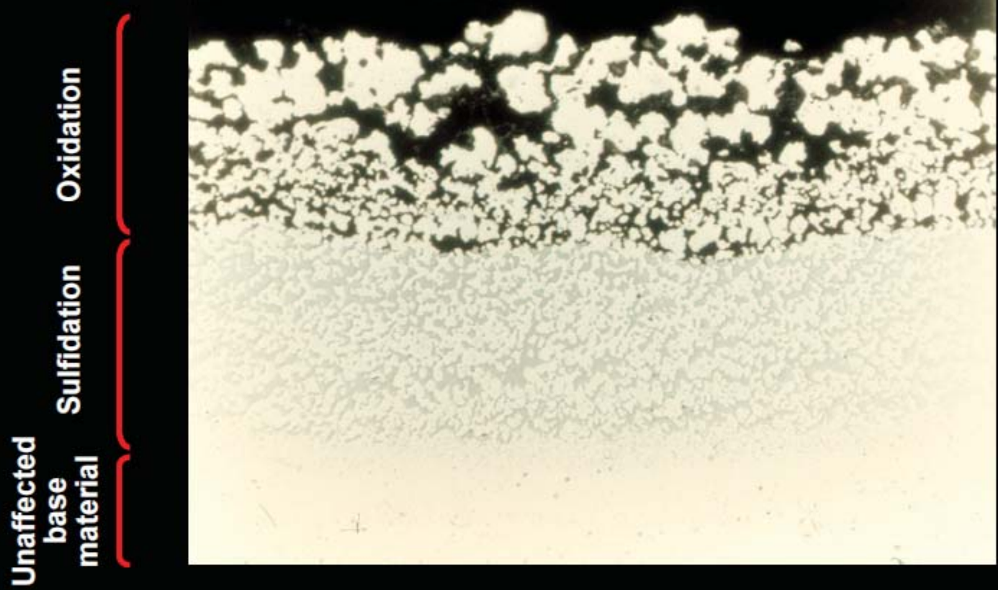


Figure 4-116 – Sulfidation failure of NPS 8 carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.



Austenitic stainless steel showing sulfidation (grey phase)

S combines with the Ni and Cr, leaving behind Fe which is not oxidation resistant, causing oxidation on the surface

Result: combined oxidation and sulfidation

- **S is an impurity in fuels / feedstock**
- **Fe, Ni, Co, Cr all form sulfides**
- **Reducing conditions**
  - **Most severe (H_2S)**
- **Oxidizing conditions (SO_2)**
  - **Less severe**
  - **Oxide barrier layer formed**

For increased sulfidation resistance:

- High Al, Si, Fe and Cr
- Presence of some oxygen
- Low Ni / Fe ratio

High Ni content not generally desirable for sulfidation resistance

Exception: high Ni + high Cr together
eg. 50Ni, 50Cr wrought INCONEL alloy 671; cast IN-657

Nitridation

Highlights:

1. Nitridation usually occurs cs, low alloy steel and ss are exposed to an ammonia bearing environment at elevated temp
2. The end surface result is hardened surface in which chromium is tied up in form of nitrides.
3. Nitriding begins above 600°F (316°C) and becomes severe above 900°F (482°C).
4. High gas phase nitrogen activity (high partial pressures of nitrogen) promotes nitriding.
5. A loss of high temperature creep strength, ambient temperature mechanical properties (specifically toughness/ductility), weldability and corrosion resistance may result.

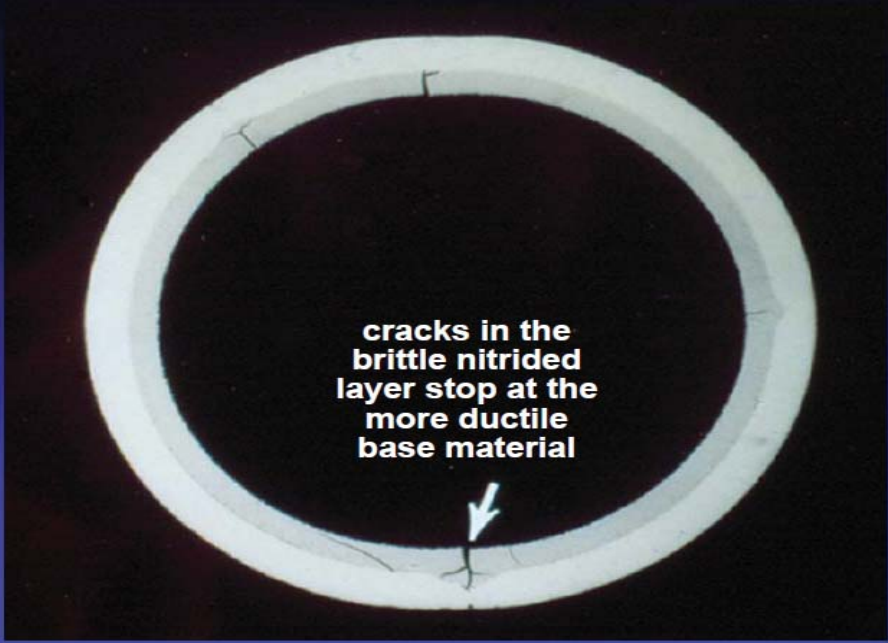
Highlights:

6. 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.

7. 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.

8. Hardness testing of the affected surfaces (400 to 500 BHN or higher) can help indicate nitriding.

9. Nitrided layers are magnetic. Therefore, 300 Series SS should be checked for magnetism as an initial screening.



Type 304 stainless steel transfer pipe in an ammonia plant
Grey area is the nitrided layer