Lecture 11:
Stainless Steels

Mmat 380

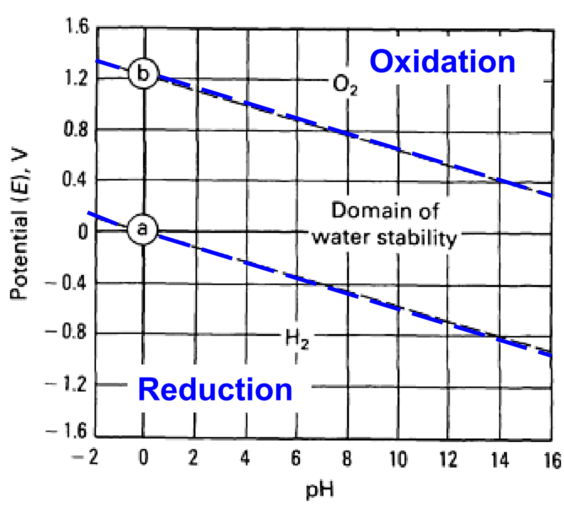
Topics to be covered

- Passive surface oxide layer and Cr
- Purpose of Ni addition
- Susceptibilities (failure mechanisms)
- Other alloying elements and their purposes
- Production of stainless steel: 6 types

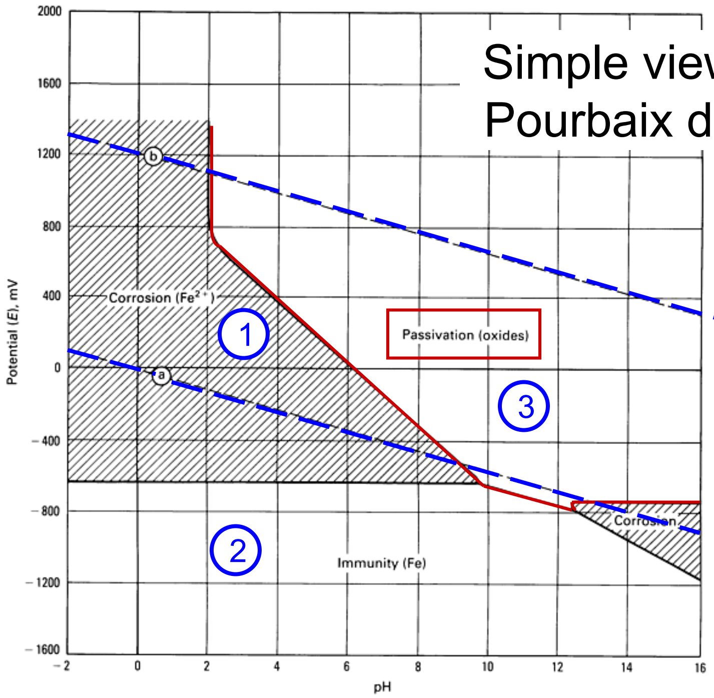
Passive surface oxide layer and Cr

- Based on formation of Cr_2O_3
  - Similar to other fairly reactive metals: Ti, Al
- Can put Fe into passive region on Eh/pH and form protective Fe oxide surface layer: anodic protection
  - Need oxidizing atmosphere to **maintain** the protective layer
  - reducing agents will destroy film and cause corrosion same as C-steel

Pourbaix diagrams: brief introduction



Simple view of Fe Pourbaix diagram



Pourbaix diagrams – 3 regions

1) **The corrosive region:** the most stable form is the metal cation or any non protective anion corrosion will occur until the metal is consumed

2) **The immune region:** corrosion is thermodynamically impossible

3) **The passive region:** an insoluble protective layer (hydroxide or oxide layer) is the most stable form; initial corrosion will occur until a protective layer is formed

Iron Pourbaix Diagram

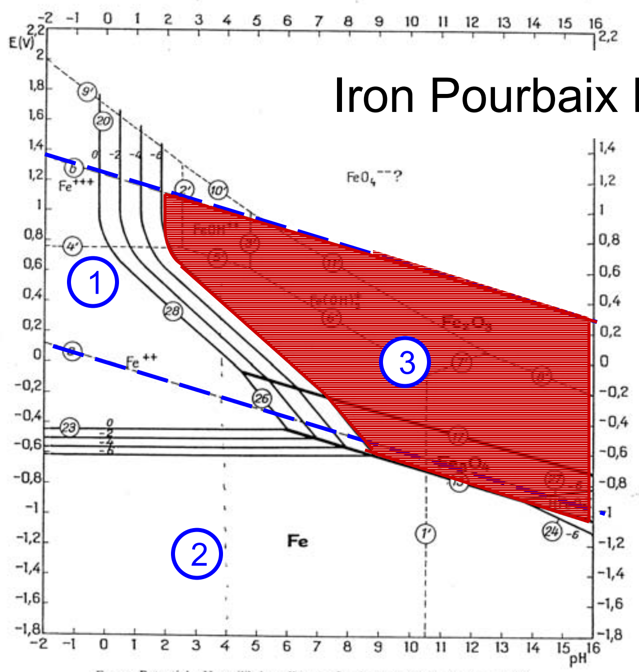


FIG. 4. Potential–pH equilibrium diagram for the system iron–water, at 25°C (considering as solid substances only Fe, Fe_3O_4 and Fe_2O_3).

Chrome Pourbaix Diagram

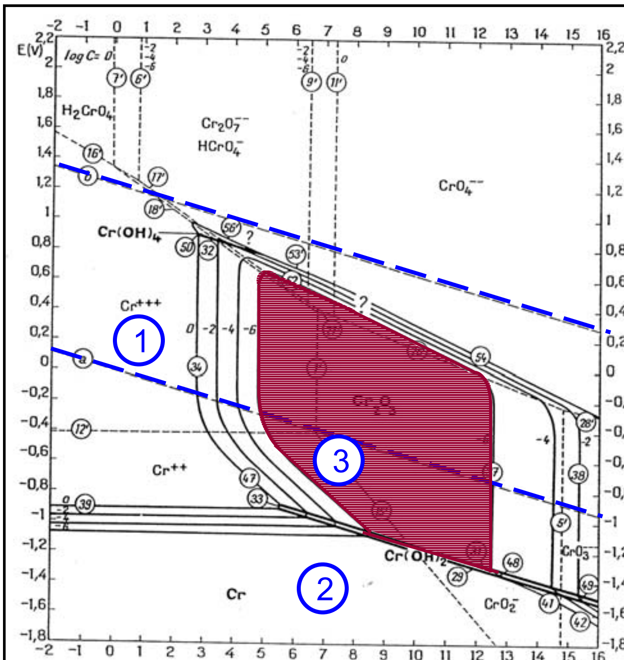
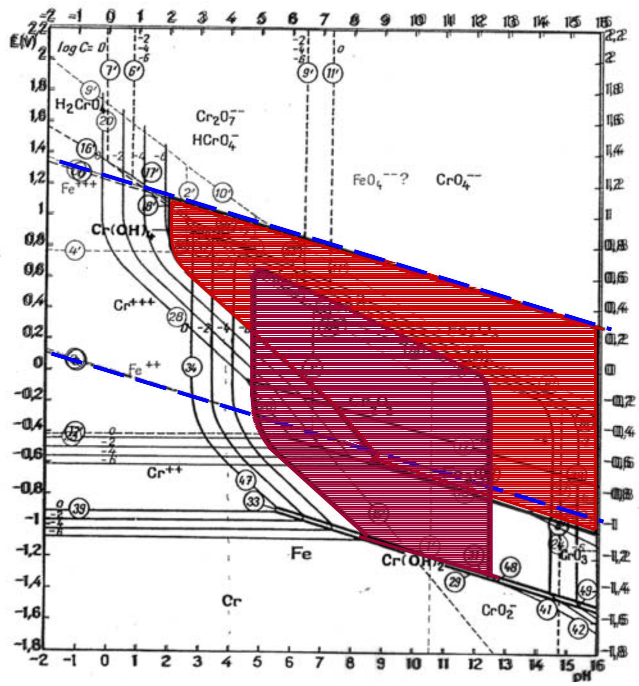


FIG. 3. Potential–pH equilibrium diagram for the system chromium–water, at 25°C. In solutions not containing chloride. (Figure established considering anhydrous Cr_2O_3.)



Overlay of Fe and Cr Pourbaix diagrams

Cr in steel

- Minimum of 12% Cr required **for passive layer:** the more Cr the better
  - Is stainless steel if : 12>%Cr>30
  - Most common : 16>%Cr>22
- If too high: can get brittle σ phase formation

Polarisation curves: brief introduction

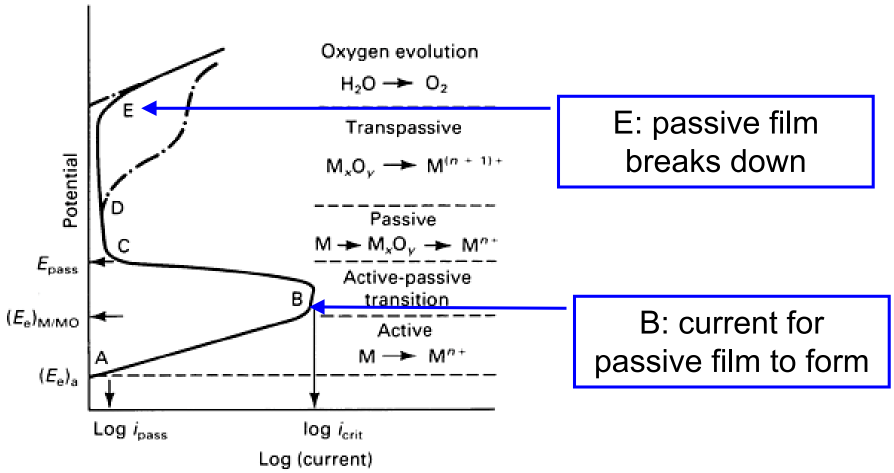


Fig. 14 Polarization curve for a metal/metal ion system that undergoes an active to passive transition

Minimum 12%: Anodic Polarisation Curves

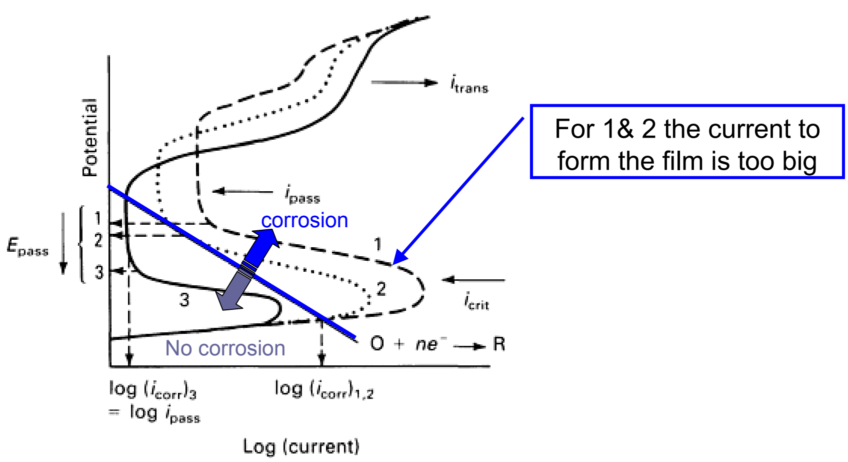
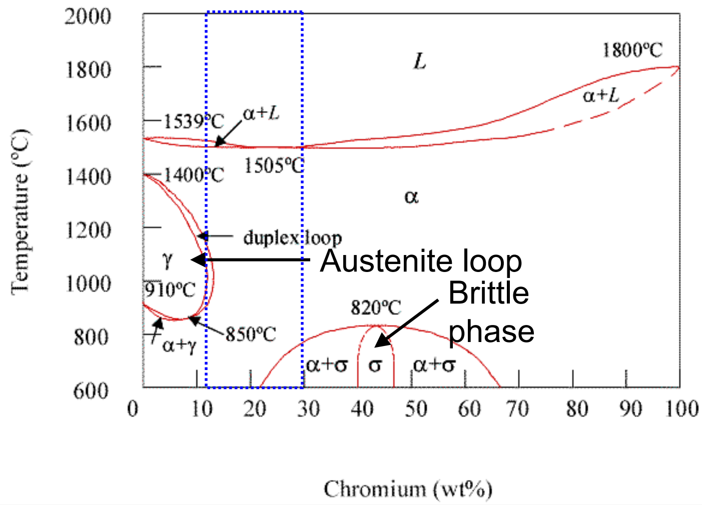


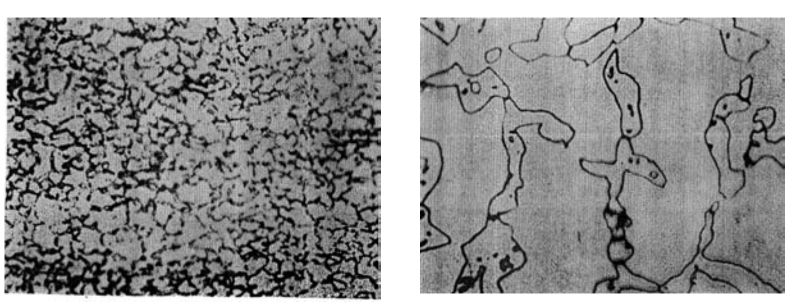
Fig. 8 Schematic anodic polarization diagrams for stainless steels containing various amounts of chromium. **(1) 3% Cr; (2) 10% Cr; (3) 14% Cr**. The polarization curve for the cathodic reaction O + ne^- R is also shown. Arrows indicate the effect of chromium addition on i_{crit}, E_{pass}, i_{pass}, and i_{trans}.

Maximum 30%: Sigma formation on Fe-Cr phase diagram



Precipitation of Sigma phase (σ-phase) in ferrite matrix

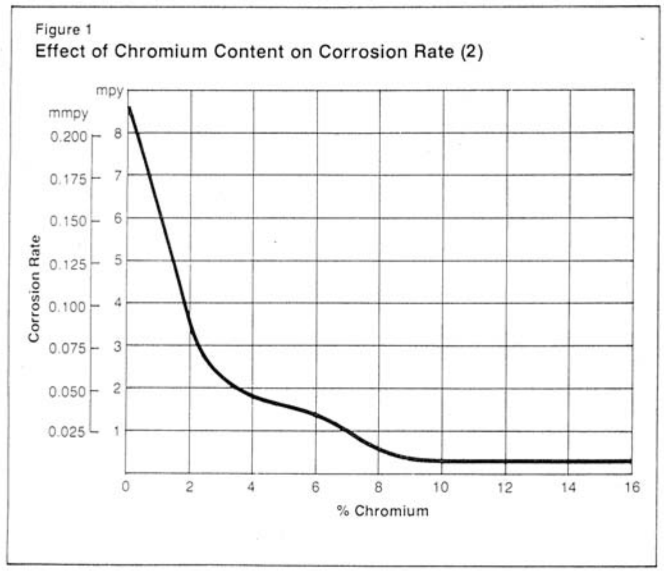
- Fe- 27%Cr ferritic stainless steels heated for 131 days @ 565^{o}C



200x

1000x

Corrosion rate vs wt% Cr



Purpose of Ni addition

- up to 25% Ni added
- More formable austenitic FCC phase instead of BCC formed
  - Only minor corrosion/oxidation resistance increase

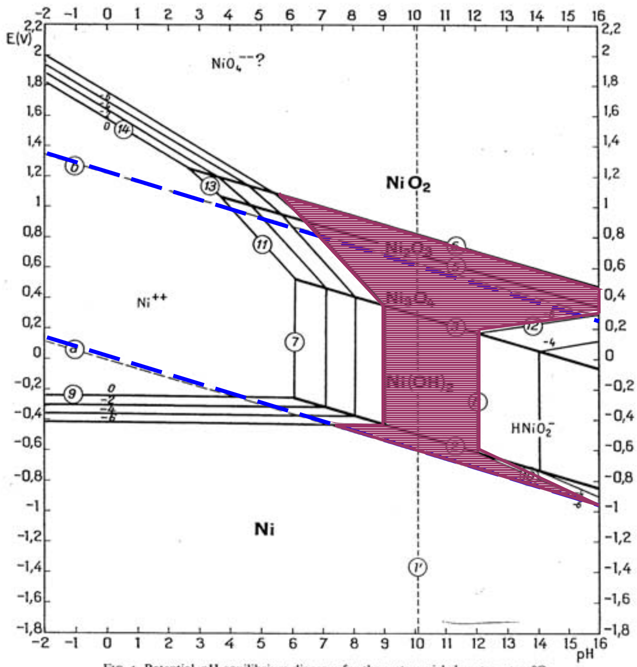
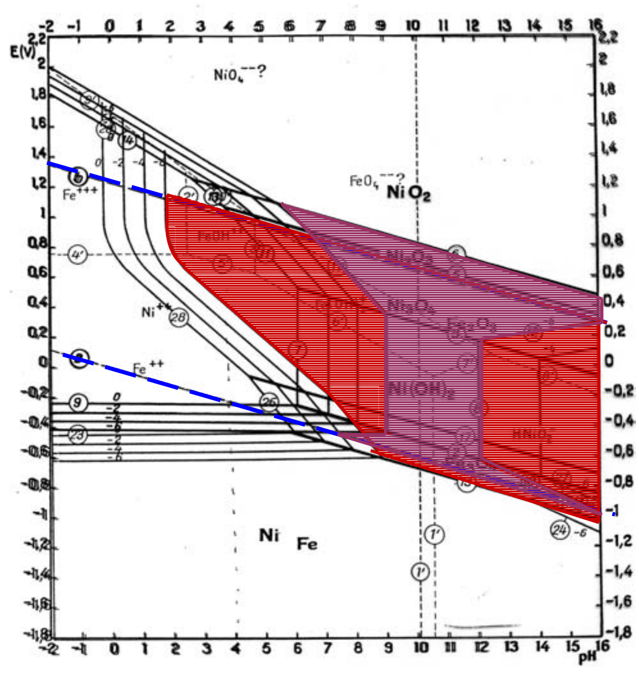


FIG. 1. Potential–pH equilibrium diagram for the system nickel–water, at 25°C.

Nickel Pourbaix Diagram



Overlay of Ni and Fe Pourbaix diagrams

Susceptibilities (failure mechanisms)

- Pitting: pitting resistance index
- Crevice corrosion
- Intergranular corrosion – weld decay
- Stress corrosion cracking

Note:

SS not always better than C-steel as can get selective attack/cracking,

Localized attack of passive layer can be catastrophic. Main culprit: Cl^- so beware of proper grade selection for coastal regions.

1. Pitting

- Passive layer attacked locally
  - Cl^- ion and others
- Deep localized corrosion

Increased tendency with:

- Increasing Cl^-
- Increasing T
- Decreasing pH
  - (increasing acidity)

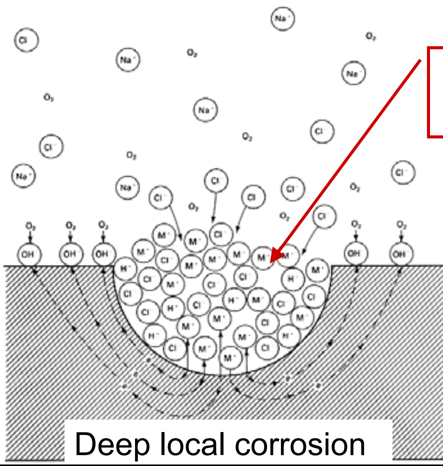
Decreased tendency with:

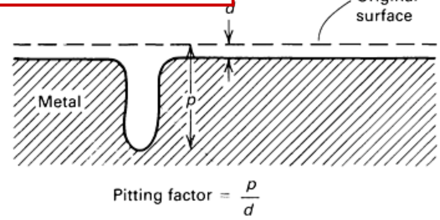
- Increasing %Cr
- Increasing %Mo
- Increasing %N

1. Pitting

- Pitting Resistance Index

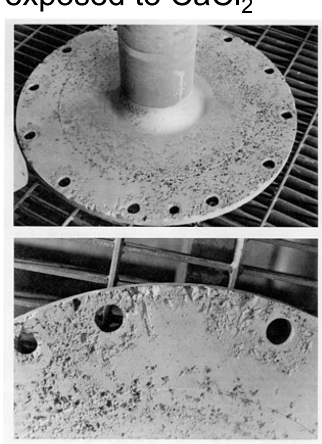
PRE=%Cr+3.3%Mo+18%N

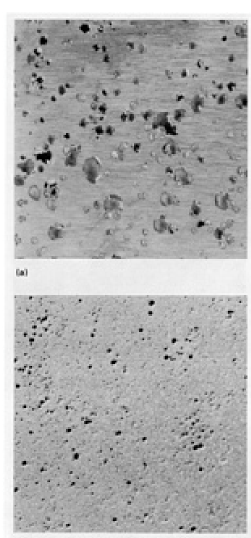




Examples of Pits

Pitting in centrifuge exposed to $CaCl_2$





Deep pits

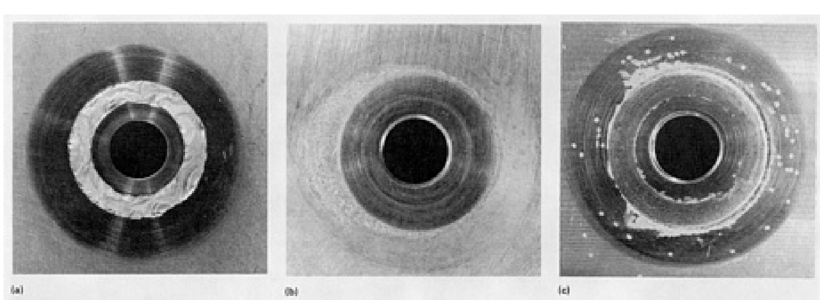
Shallow pits

2. Crevice Corrosion

- Similar to pitting (area with high local conc.)
- Oxygen cells:
  - Low [O] areas corrode: anodic
  - High [O] areas protected: cathodic
    - Note:
    - anodic rxn: oxidation: production of e^-
    - Cathodic rx: reduction: consumption of e^-
  - Bolted connections susceptible,
  - under dirt, scale etc.

Want: open shallow crevices: continued entry of bulk environment, weld overlay with more corrosion-resistant alloy in some cases or cathodic protection

Examples of Crevice Corrosion



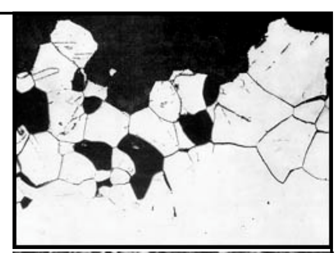
Crevice-related corrosion for different alloys in natural seawater. (a) Alloy 904L (20Cr-25Ni-4.5Mo-1.5Cu) after 30 days. (b) 70Cu-30Ni after 180 days. (c) Alloy 400 (70Ni-30Cu) after 45 days

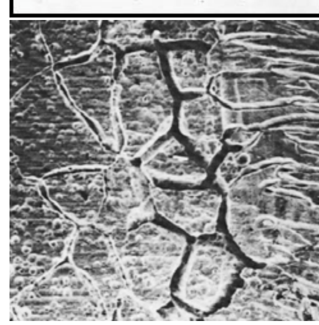
Factors that can affect the crevice corrosion resistance of stainless steels

geometrical	**Metallurgical**	**Environmental**	**Electrochemical reactions**
Type of crevice: metal to metal nonmetal to metal Crevice gap (tightness) Crevice depth Exterior to interior surface area ratio	Alloy composition: major elements minor elements impurities Passive film characteristics	Bulk solution: O_2 content pH chloride level temperature agitation Mass transport, migration Diffusion and convection Crevice solution: hydrolysis equilibria Biological influences	Metal dissolution O_2 reduction H_2 evolution

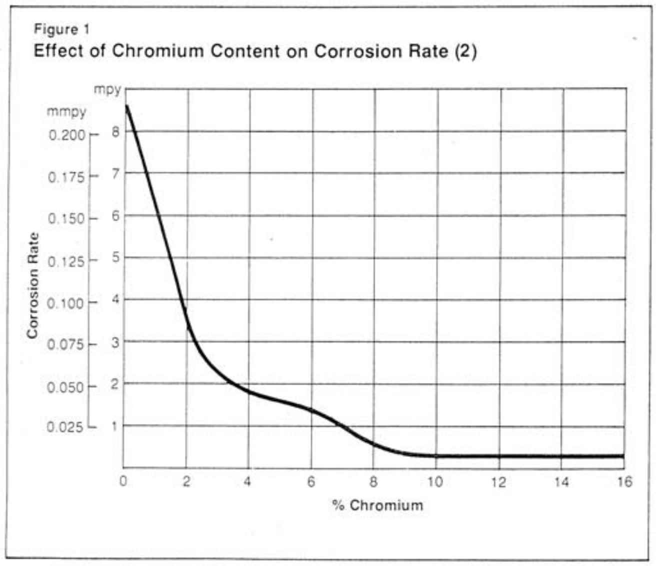
3. Intergranular corrosion

- If held 400-850^{o}C region: CrC ppt occurs on grain boundaries: $Cr_{23}C_6$
- Depletes adjacent areas of Cr
- Grain boundary corrodes
  - Also referred to as **Weld decay** and **Sensitization**

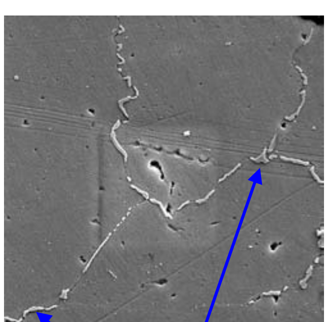


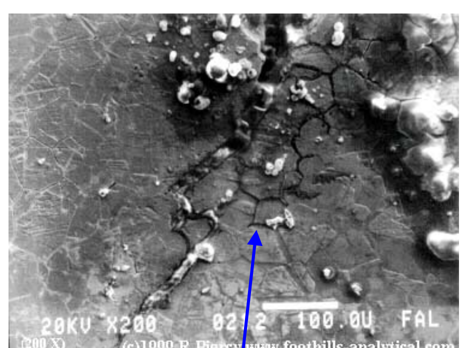


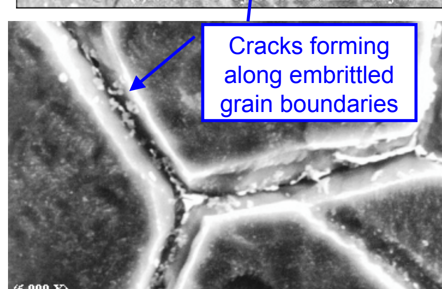
Corrosion rate vs wt% Cr



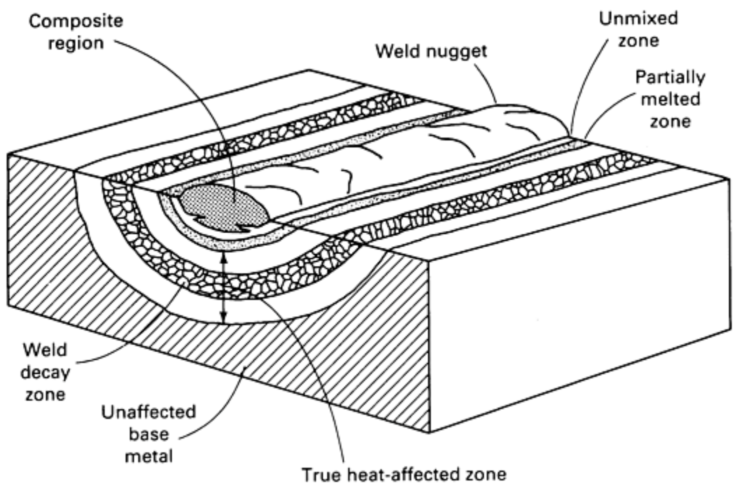
Chromium carbides at grain boundaries







Weld Segment: sensitization/weld decay



Polarisation curves: brief introduction

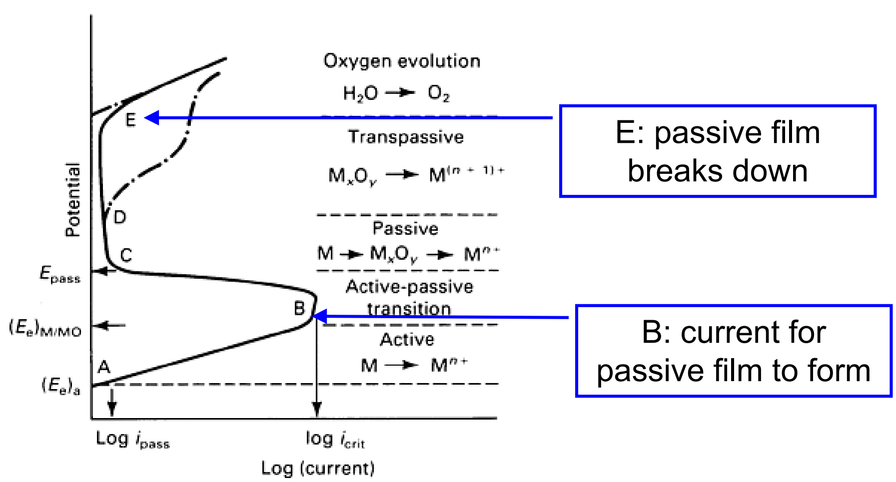
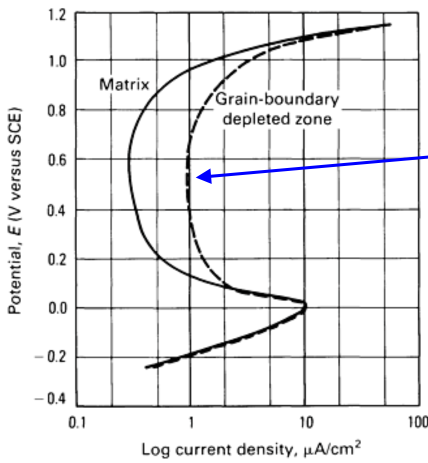


Fig. 14 Polarization curve for a metal/metal ion system that undergoes an active to passive transition

Anodic polarization in sensitized alloy



Higher current; more corrosion, in depleted zone

Fig. 1 Anodic polarization behavior of an active-passive alloy with grain-boundary depleted zones (schematic)

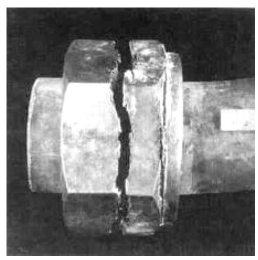
3. Intergranular corrosion

Decrease by:

- increasing %Cr
- Stabilizing by adding Ti or Nb/Ta (stronger carbide formers)
- Decreasing %C
- Heat treat to 1050°C to redissolve carbides and quench through sensitized temperature region

4. Stress corrosion cracking

- Branched
- Stress (residual or applied
- Contain ionic species
- Cl^- and OH^- for stainless steel



Other alloying elements and their purposes

Element	Amount (%)	Purpose
Cr	12-30	Cr_2O_3 – gives stainless character, stabilises α phase
Ni	0-25	Stabilises γ phase (FCC)
Mo	0-9	Reduces pitting and crevice corrosion: stabilises γ-phase
N	<0.5	Reduces pitting/crevice corrosion; stabilizes γ-phase
Ti, Nb	<1	Strong carbide formers; reduce sensitization
C	<0.15 except martensitic grades	Hard martensite for cutting edges; stabilizes γ-phase
Mn	0-12	Ni replacement; stabilizes γ-phase

Production of Stainless Steels

Types	Major Alloy Additions	AISI
• Ferritic - α	Fe-Cr	4xx
• Martensitic	Fe-Cr-C	4xx
• Austenitic - γ	Fe-Ni-Cr	3xx
• Duplex ($\alpha+\gamma$)	Fe-Cr-Ni	
• Precipitation hardened	Fe-Cr-Ni	
• Super ferrites & austenitics	Higher alloy versions of 1 & 3	