

Chemical Engineering 378

Science of Materials Engineering

Lecture 31

Corrosion: Protection

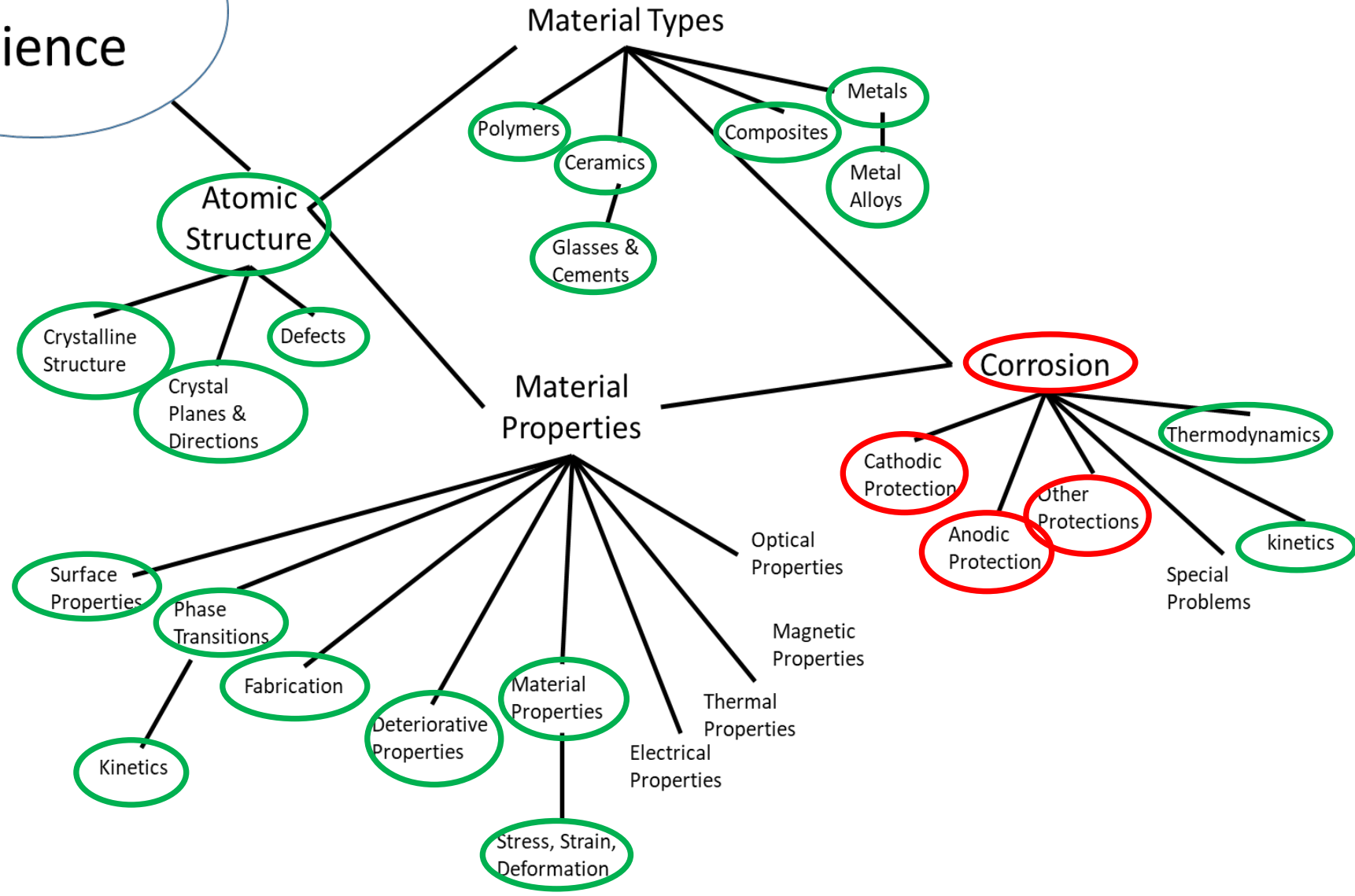


Spiritual Thought

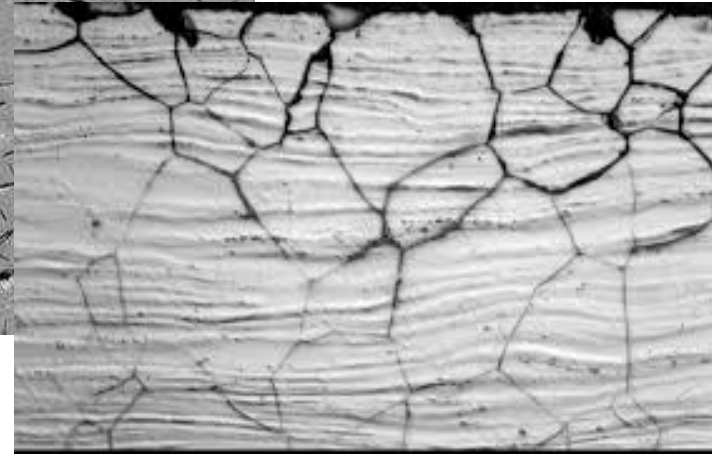
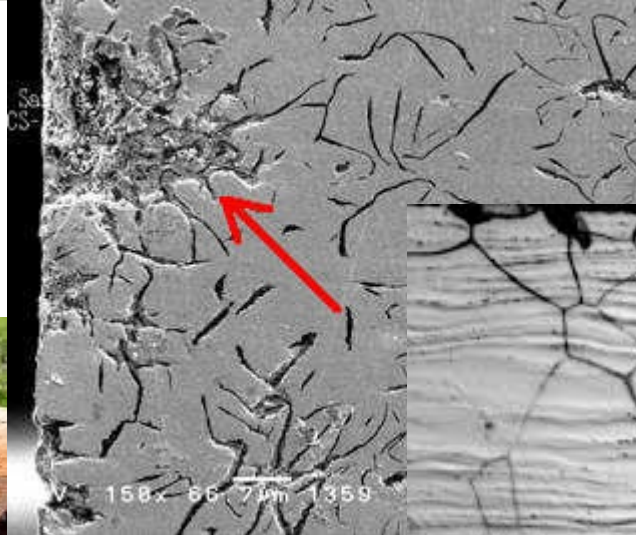


Materials Roadmap

Materials Science



Corrosion Types



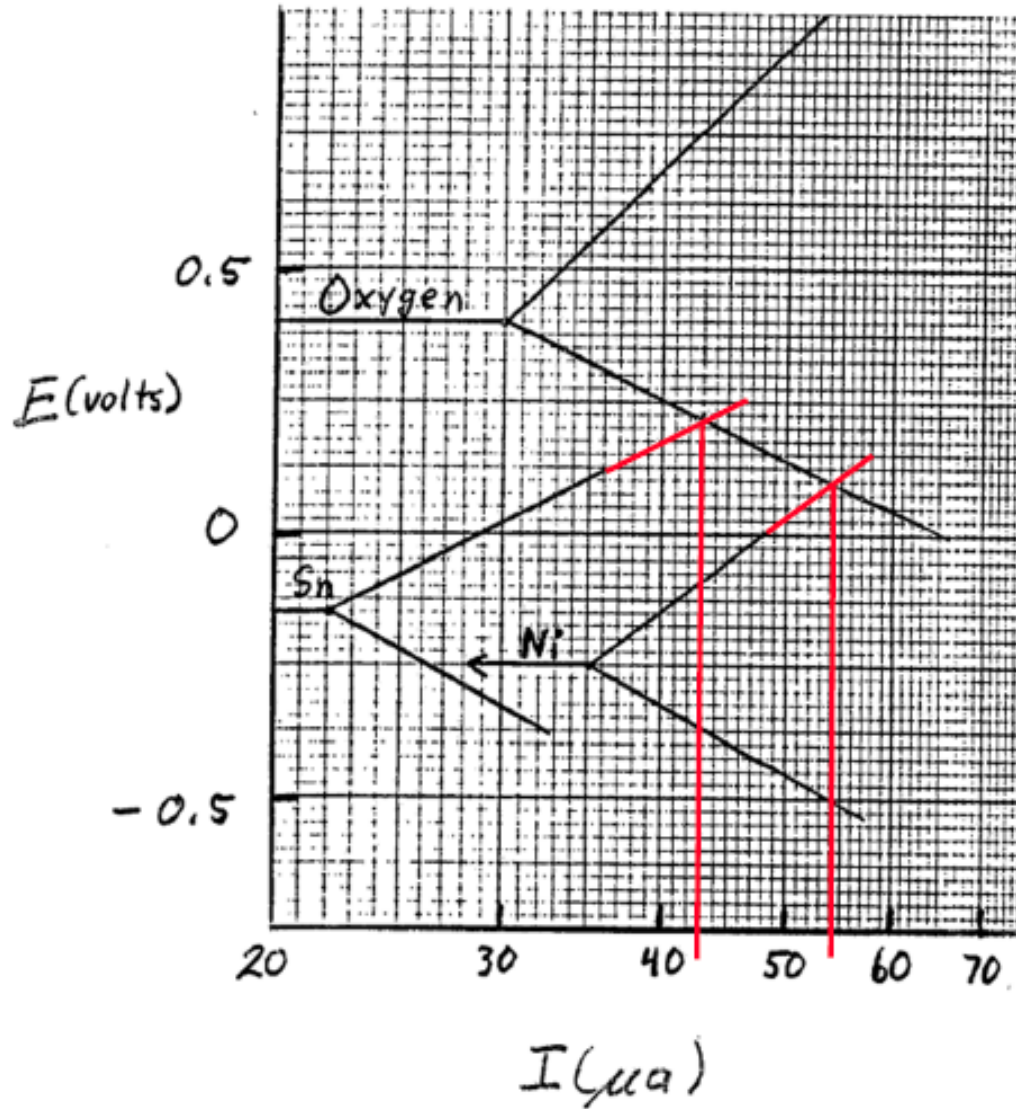
Example

A tin rod and a nickel rod are both in a basic aerated solution but are not touching each other. The rods are 1.0 cm in diameter and 20 cm long. The current distributions are essentially the same in both rods, and the currents for the corrosion half-reactions are shown on the accompanying figure.

- A. Which rod corrodes at the fastest rate?
- B. What is the corrosion current density for the nickel rod?
- C. What is the corrosion rate of the nickel rod in g/yr and mm/yr?
- D. What would happen to the corrosion of each rod if the rods touch?



Solution



Solution (cont)

A. Nickel: $I_c = 54 \mu\text{a} > \text{Tin: } I_c = 43 \mu\text{a}$

B. Area = $2\pi r^2 + \pi dL$

$$= 2\pi(0.5 \text{ cm})^2 + \pi(1\text{cm})(20\text{cm}) = 64.4 \text{ cm}^2$$

$$i_c = I_c/A = (54 \mu\text{a})/(64.4 \text{ cm}^2) = 0.838 \mu\text{A/cm}^2$$

$$\text{C. } r = I/nF = \frac{(54 \times 10^{-6} \text{ C/s}) (58.69 \text{ g/mol})}{2 (96,500 \text{ C/mol})}$$

$$= 1.64 \times 10^{-8} \text{ g/s} \times (3600\text{s/hr})(24\text{hr/day})(365\text{days/yr})$$

$$= 0.518 \text{ g/yr} \times (10\text{mm/cm})/[64.4\text{cm}^2)(8.9\text{g/cm}^3)]$$

$$= 9 \times 10^{-3} \text{ mm/yr}$$

D. Galvanic couple: Nickel becomes anode and corrodes at $31\mu\text{a}$, Tin is cathode



CORROSION PREVENTION (I)

- Materials Selection

- Use metals that are relatively unreactive in the corrosion environment -- e.g., Ni in basic solutions

- Use metals that **passivate**

- These metals form a thin, adhering oxide layer that slows corrosion.



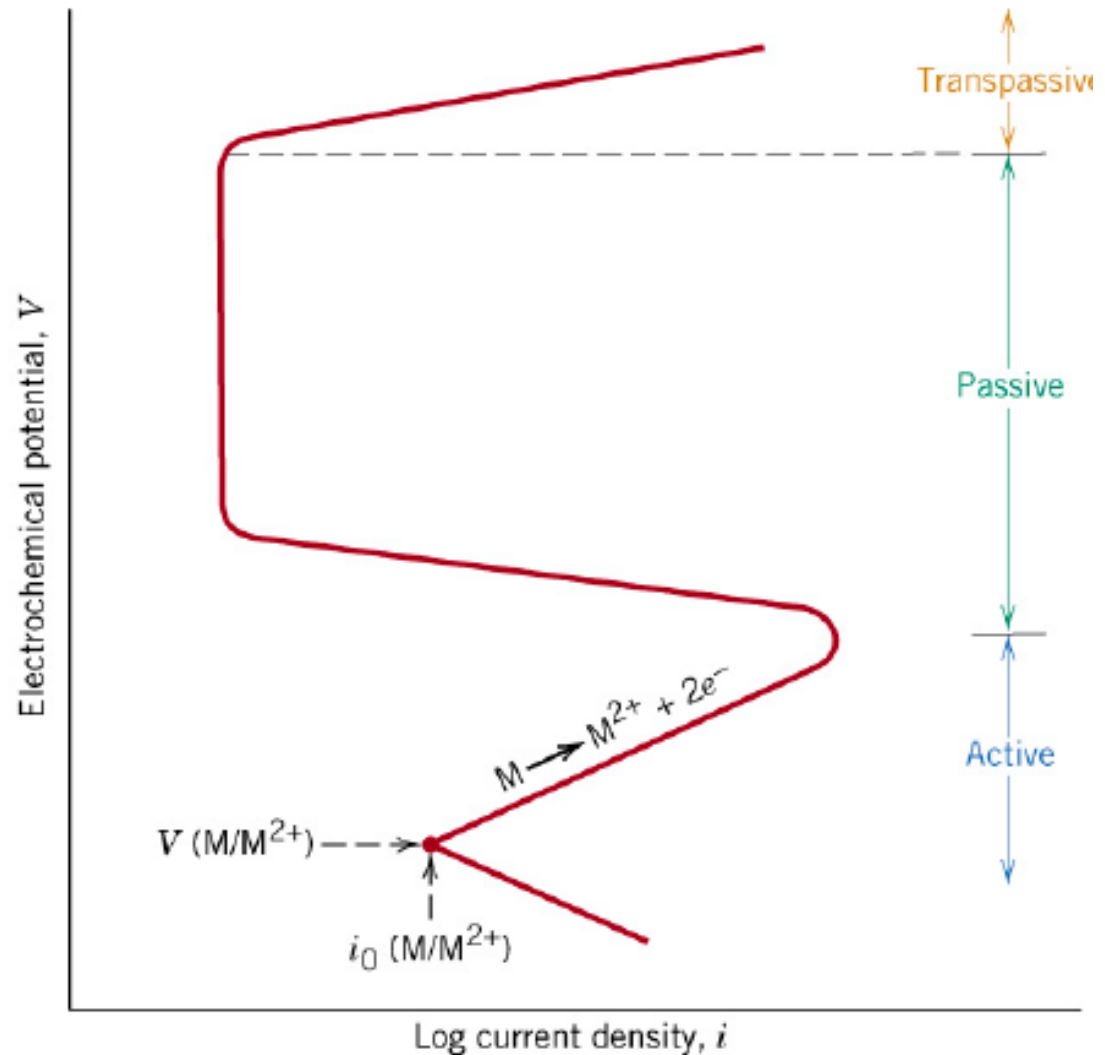
Metal oxide
Metal (e.g., Al,
stainless steel)

- Lower the temperature (reduces rates of oxidation and reduction)
- Apply physical barriers -- e.g., films and coatings

Passivation

- Corrosion current density is greatly reduced in the passivated (inactive) state.

Fig. 16.12, Callister & Rethwisch 3e.



Passivation (cont)

- Stronger reducing reactions actually produce lower corrosion rates

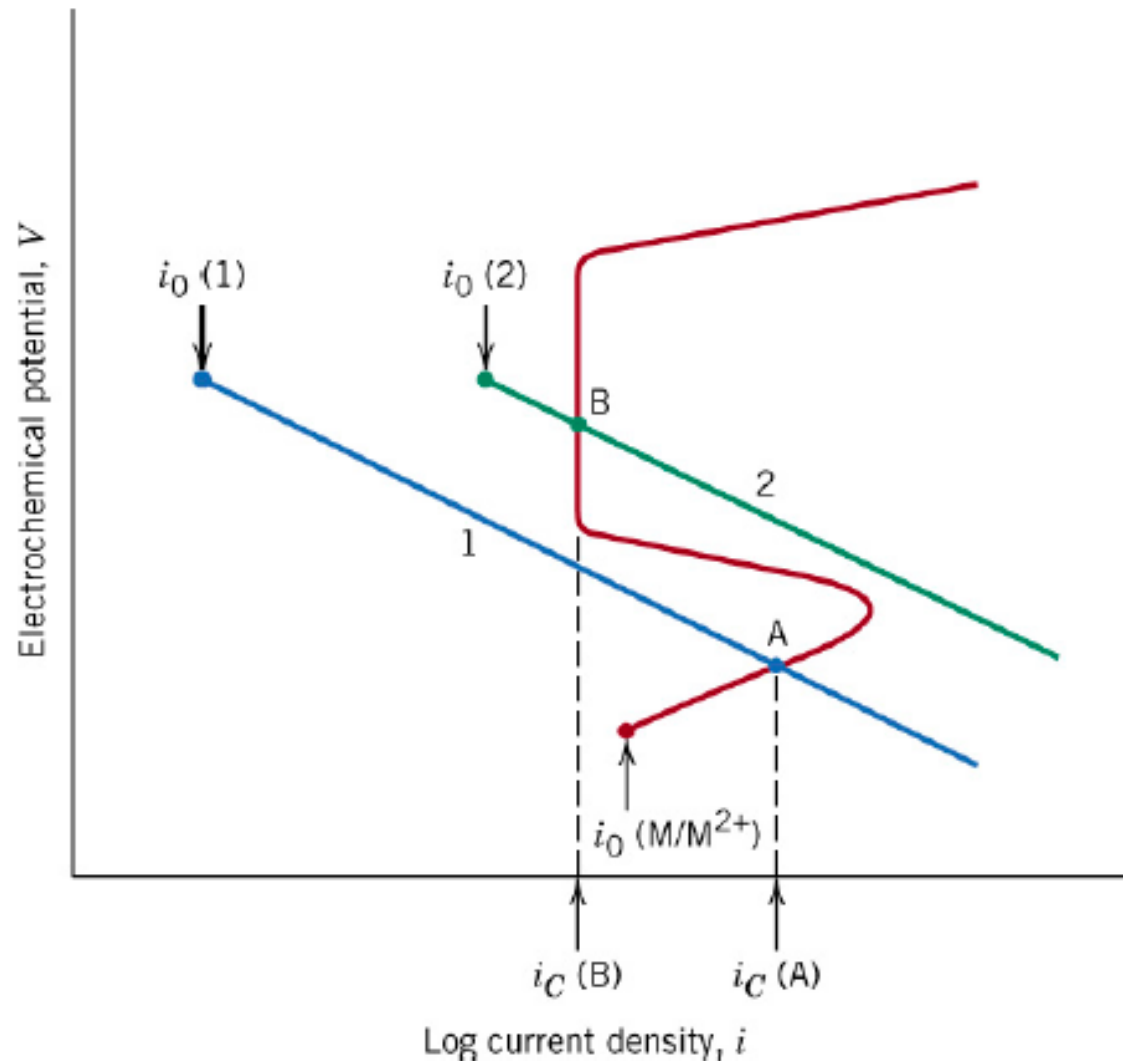
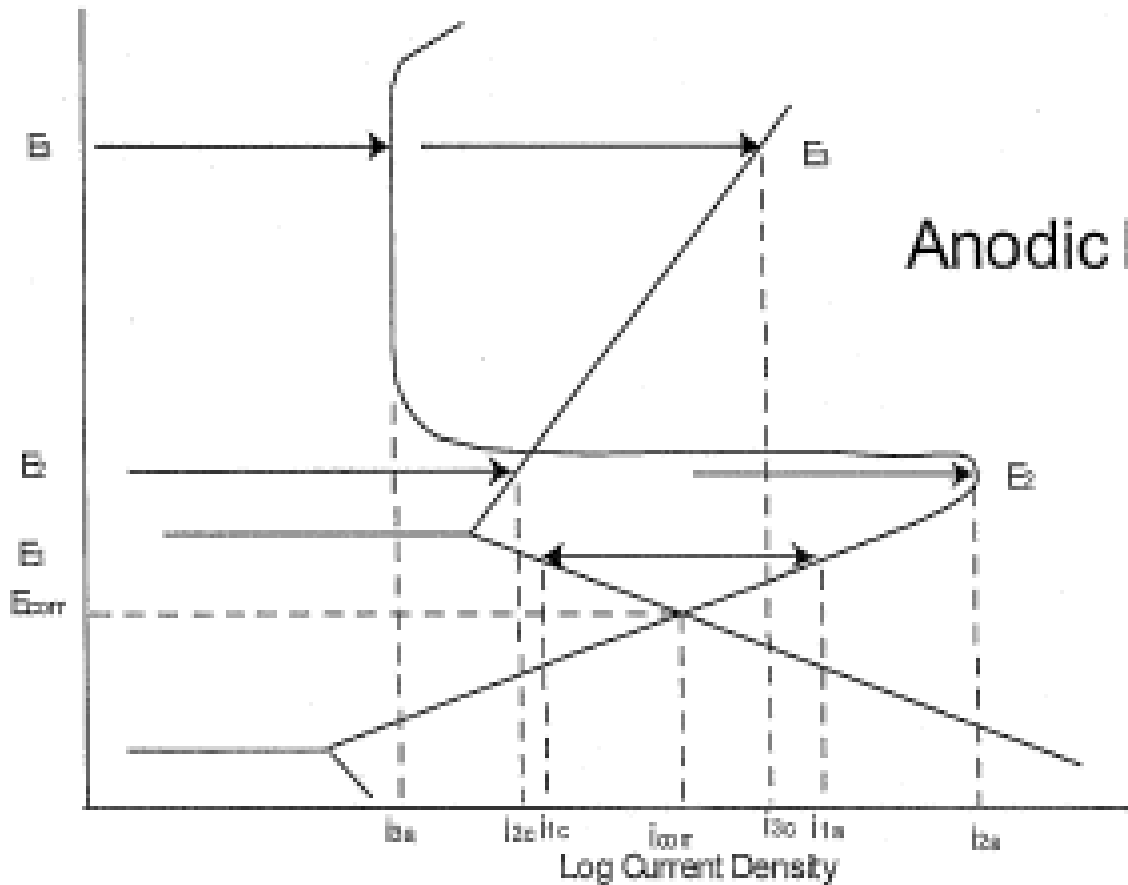
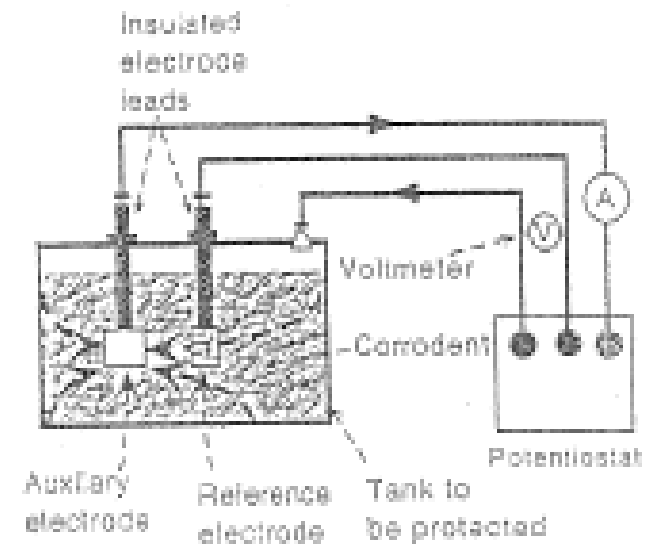


Fig. 16.13, Callister & Rethwisch 3e

Anodic Protection



Anodic Protection



Passivation (cont)

- Oxides inhibit corrosion if they...
 - Form thin stable passivating films
 - Form thick *stable* scales

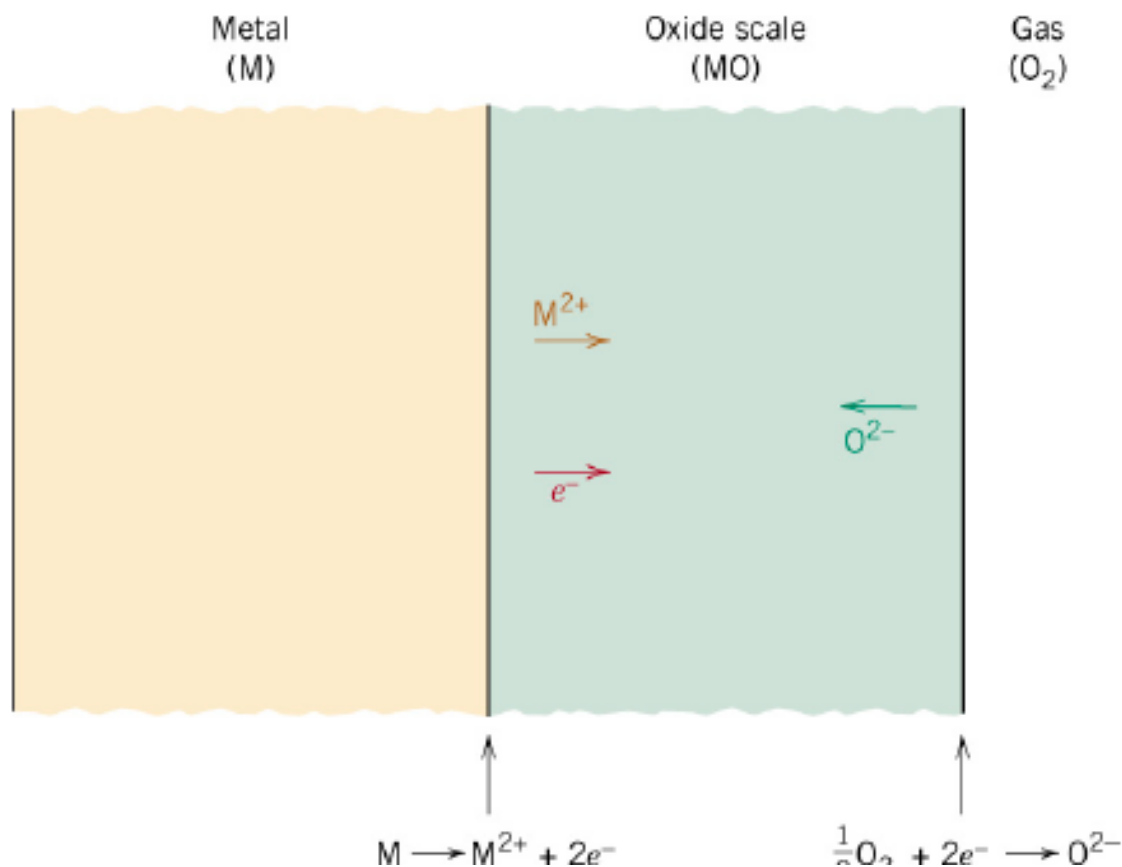
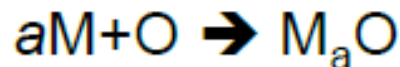


Fig. 16.24, Callister & Rethwisch 3e

Oxide Layers

- Oxides won't inhibit corrosion if they...
 - Cover imperfectly (expose bare metal)
 - Break off



$$\text{Pilling-Bedworth ratio} = \frac{\text{Volume per mole oxide}}{a(\text{Volume per mole metal})} = \frac{(\text{Mol.wt.} / \rho)_{\text{oxide}}}{a(\text{At.wt.} / \rho)_{\text{metal}}}$$

- Principle: If the P-B ratio $< \sim 0.6$, oxide covers imperfectly
If the P-B ratio $> \sim 2.0$, oxide breaks off
- Affected by oxide bonding, oxide ductility, etc.



CORROSION PREVENTION (II)

- Lower the temperature (reduces rates of oxidation and reduction) – may not be possible
- Reduce flow impaction (erosion)
- Reduce crevices (e.g. weld vs. bolts/rivets)
- Reduce stresses
 - Applied stresses
 - Residual stresses (e.g. anneal)



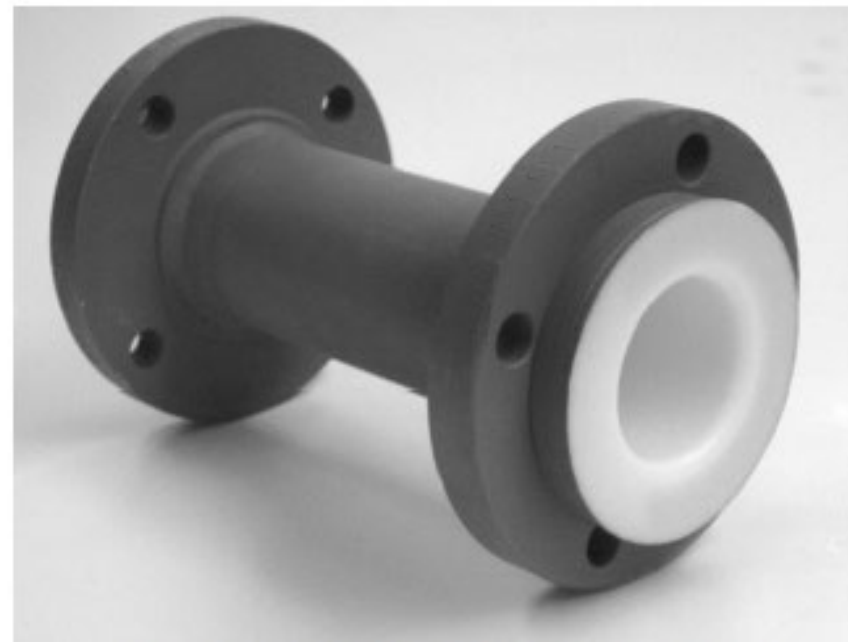
CORROSION PREVENTION (III)

Apply Physical Barriers

- Thin physical barriers -- e.g., films, coatings, paint
 - If the cathode and anode are separate and you can only paint one... which one do you paint?
 - Hint: all coatings and paints have pin-hole flaws (want to change your answer?)
 - Answer: paint the **cathode**!
(if you can paint both, paint the anode also)
- Thick physical barriers -- e.g., linings



Protective Layers



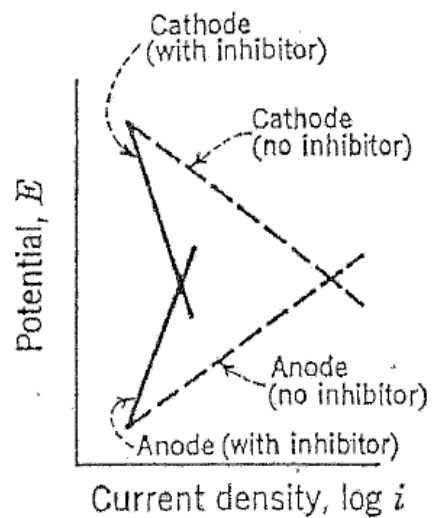
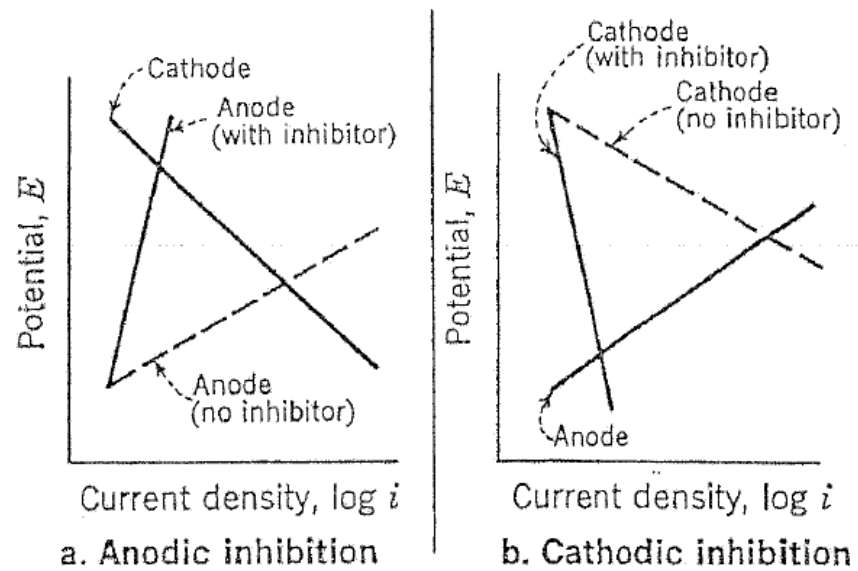
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<http://image.made-in-china.com/2flj00UCdQwWKrbYkf/Steel-Liner-Teflon-Polypropylene-Compound-Tube.jpg>

Inhibitors

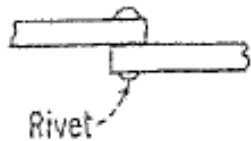
- Anodic:
 - Oxidizing agents that promote passivity: chromates, nitrates, ferric salts
 - Insoluble films: alkalis, phosphates, silicates
- Cathodic:
 - Oxygen scavengers: sodium sulfite, hydrazine
 - Poisons for hydrogen evolution: arsenic, antimony, bismuth, sulfur
 - Insoluble films: calcium bicarbonate
- Both:
 - Adsorption inhibitors: amines (used in the oil industry to convert H_2S to polyamines)
 - Volatile amines are also used in boilers to minimize effects of acids: amine salts, morpholine, sodium benzoate





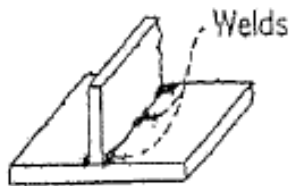
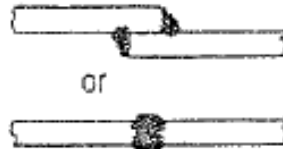
Best Practices (welding)

Poor Design

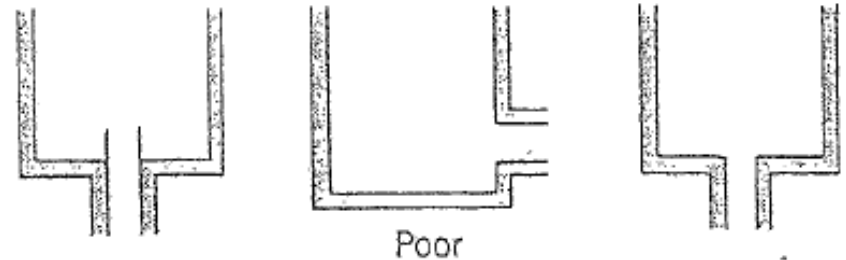
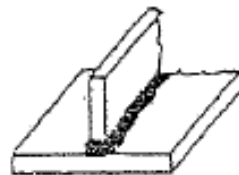


Avoid
crevice by:

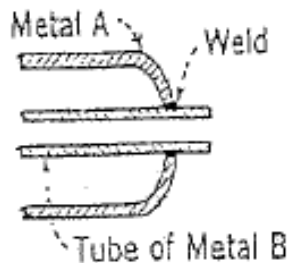
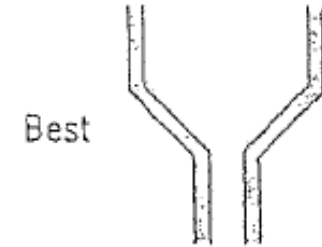
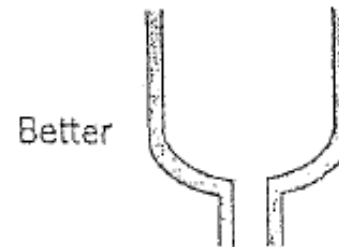
Good Design



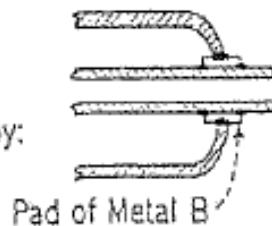
Avoid
crevice by:



Avoid end-grain
attack by:



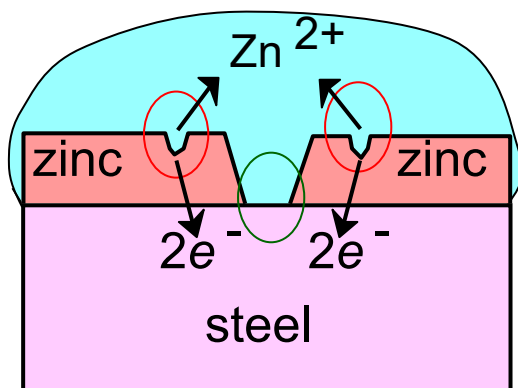
Avoid dilution
of Metal B
by A at weld by:



CORROSION PREVENTION (IV)

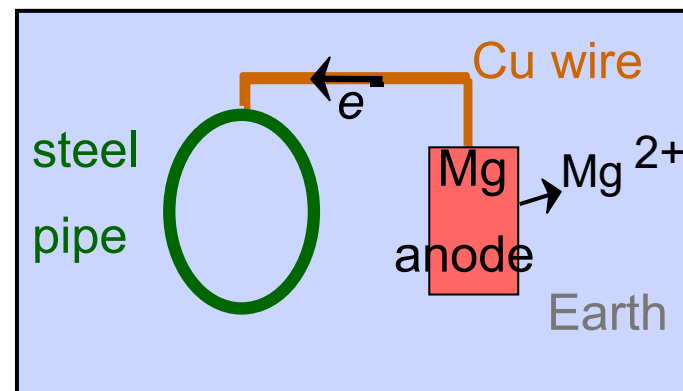
- Cathodic (or sacrificial) protection
 - Attach a more anodic material to the one to be protected.
 - Apply a current

Galvanized Steel



e.g., zinc-coated nail

Using a sacrificial anode



e.g., Mg Anode

SACRIFICIAL ANODE

Marine applications

Ships



Piers



Concrete Piling
with Steel
Reinforcement

Cast Fiberglass
Jacket with Zinc
Anode