

**16.1** Steel products are commonly protected by chromium or zinc coatings. Based on the galvanic series, what difference would you expect in their ability to protect steel?

Zinc is anodic to steel. A coating of Zn will continue to protect the underlying steel even in the presence of a scratch in the coating that exposes steel.

Chromium is cathodic to steel. Thus, if the chromium coating has a scratch, the underlying steel will corrode. Chromium plating is commonly used because of its aesthetic appearance.

**16.2** Explain why a small anode/cathode area ratio will result in a higher corrosion rate.

Recall that any corrosion reaction involves a flow of current. The corrosion rate is proportional to the current density. Thus, for a given current, a small anode/cathode area ratio will result in a higher current density at the anode than for a large ratio anode/cathode ratio, i.e., a small anode/cathode area ratio will lead to a higher corrosion rate.

**16.3** Alclad aluminum consists of a thin layer (5--10% of total thickness) of one Al alloy metallurgically bonded to the core alloy. Generally, the cladding layer is anodic to the core. Why?

When two dissimilar metals are separated by an electrically conducting compound (molten or in solution) called an electrolyte, there develops a voltage difference. The electrolyte conducts current by movement of ions. If we connect the two metal electrodes by a wire, the circuit is closed and an electric current flows. This is the basis of galvanic corrosion. Alclad (a trademark of Alcoa) is a generic term that describes aluminum surface layers bonded to a high strength aluminum alloy core. The cladding, generally pure aluminum is anodic to the core to protect the high strength core alloy. The result is corrosion-resistant high strength aluminum alloy.

**16.4** Tinplate (commonly used in the canning industry) is not plate or sheet of tin. It is actually a steel strip with a thin coating of tin. Discuss the pros and cons of using tin to protect steel.

Tin coating on steel merely isolates it from the electrolyte and thus protects it from corrosion. It is important to note that steel is anodic with respect to tin, so if the tin coating is accidentally scratched, rapid corrosion of the underlying steel will occur. Thus, a tin coating will protect the underlying steel as long as it covers the steel perfectly. Coating with a plastic such as epoxy will do the same job.

The main reason a tin coating is used to protect the steel foil, used mostly for food cans, is that tin is not toxic while zinc is. However, if the tin coating on a food can gets scratched and rust appears, it is not advisable to eat the food in the can. Commonly, tinplating is done by passing the thin steel sheet through an electrolytic bath and tin is deposited on both sides of the sheet.

**16.5** Describe how galvanizing (coating steel with zinc) works as a cathodic protection for steel.

Zinc coating on steel (called galvanized steel) also protects the steel. Unlike tin (see problem # 16.5), steel is cathodic with respect to zinc, i.e., zinc is anodic with respect to steel. Thus, if the zinc coating is scratched, a small area of cathodic steel will be exposed and will result in slow corrosion of the zinc coating.

**16.6** Describe some methods of protecting the inside of a metallic pipe against chemical attack.

Following are some common ways of protecting a metallic pipe against chemical attack.

Different forms of cathodic protection are commonly used to protect steel pipes.

1. Make the metallic pipe (commonly steel) to be cathodic by connecting a sacrificial anode (commonly zinc or magnesium). The sacrificial anode is made of a metal (e.g. zinc anodes for steel) that is higher in the electrochemical series than the item to be protected.
2. For larger pipeline structures, a system called impressed current cathodic protection is commonly used. A direct current (DC) power source called a rectifier is connected between an anode (commonly a scrap iron piece) and the buried pipeline which acts as a cathode. The scrap iron anode corrodes and the pipeline is protected. Permanent impressed-current cathodic-protection system

consisting of several cathodic-protection stations located evenly (typically 1 – 2 km apart) along the pipeline operate continuously.

3. Electrical interference from the high voltage alternating current (HVAC) distribution power lines should be avoided. Induced HVAC voltage on the coated pipeline can pose hazardous step-voltage shock to the pipeline operators. This is done by installing equipotential mats and insuring proper insulation.
4. Coating with a plastic such as epoxy is another technique. Oil and gas companies around the world employ epoxy coating on steel pipes to protect against corrosion. Examples include internal and external coatings for pipelines used for natural gas, oil (petroleum), water and sewage, as well as piping in oil refineries, petrochemical plants, power plants and paper mills.
5. There is one very important problem related to items # 2 and 4 listed above. Effectiveness of impressed current cathodic protection system on steel pipelines is counteracted by the use of polymeric coatings such as epoxy and polyethylene. These polymeric coatings have high electrical resistivity. Electrical current from the cathodic protection system is blocked by the highly resistive coating, i.e., the current cannot reach the steel pipeline surface causing cathodic shielding problem. Such solid film backed coatings are largely prohibited in North America.

**16.7** A form of corrosion called pitting corrosion can occur in aluminum in fresh water. As the name suggests, pits form on the surface of aluminum in this type of corrosion. The pit depth,  $d$  follows a cube root relationship time,  $t$ :

$$d = A t^{1/3}.$$

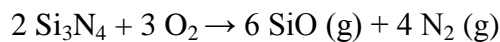
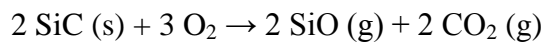
Normally, a 5  $\mu\text{m}$  thick  $\text{Al}_2\text{O}_3$  film forms on the surface of aluminum. If we double the thickness of the film, by what factor will the time to perforation increase?

$$\begin{aligned} d_1/d_2 = 2 &= (t_1/t_2)^{1/3} \\ t_1/t_2 &= 8 \end{aligned}$$

The time to perforation will increase eight fold, if we double the thickness of the coating.

**16.8** Structural ceramic materials such as SiC, Si<sub>3</sub>N<sub>4</sub>, MoSi<sub>2</sub>, etc. oxidize in the presence of oxygen at high temperatures. Give the oxidation reactions and indicate how the reaction products serve to protect these materials from further oxidation. Does it have deleterious effect on the high temperature capability of these materials?

Surface of structural ceramics such as SiC or Si<sub>3</sub>N<sub>4</sub> can get oxidized as per following reactions:



What is important to note in these reactions is that as gaseous reactions products diffuse away from the surface, the underlying ceramic gets consumed. If a protective, solid oxide layer could be formed, that would be desirable. In the case of MoSi<sub>2</sub>, a stable, protective silica coating can form which allows it to be used as a high temperature furnace element under oxidizing conditions. In the case of SiC and Si<sub>3</sub>N<sub>4</sub>, surface oxidation puts an upper limit on the use or service temperature.

**16.9** A Ni-based superalloy has 0.2 μm thick oxide layer. When placed in a burner rig to test for oxidation, it was observed to grow to 0.3 μm in 1 h. If the superalloy follows a parabolic oxidation law ( $x^2 = a + bt$ , where  $x$  is the thickness,  $t$  is the time, and  $a$  and  $b$  are constants) what is the thickness after one week?

Parabolic oxidation rate

$$x^2 = a + bt$$

At  $t = 0$ ,  $x = 0.2 \text{ μm}$ .

Therefore,

$$(0.2)^2 = a$$

$$\text{Or } a = 0.04 \text{ μm}^2$$

At  $t = 1 \text{ h}$ ,  $x = 0.3 \text{ μm}$ .

Therefore,

$$(0.3)^2 = b \cdot 1 + 0.04$$

Or

$$b = 0.05 \text{ mm}^2/\text{h}$$

Thus, at  $t = 1 \text{ week} = 168 \text{ h}$ ,

$$x^2 = 0.04 + 0.05 \times 168 = 8.44 \text{ } \mu\text{m}^2$$

Or  $x = 2.9 \text{ } \mu\text{m}$