Lecture 38

Metallurgical Properties Influencing Corrosion

Keywords: Metallurgical Properties, Intergranular Corrosion, Hydrogen Embrittlement, Iron Pillar

Metallurgical properties and structure influence corrosion in various ways.

- Sulfide inclusion causes initiation of pitting in stainless steels.
- Grain boundary segregation of phosphorous, carbon and nitrogen can cause intergranular stress corrosion cracking of carbon steels.
- Susceptibility to hydrogen cracking of steels.
- Certain metallographic structures are unfavourable - for example, martensite reduces resistance to hydrogen cracking of steels.
- Crystallographic grain orientations can influence corrosion behavior. Grain boundaries susceptible - Segregation of alloying elements and precipitates to grain boundaries creating anodic and cathodic areas.
- Different metallographic phases in an alloy may exhibit varying resistance to corrosion.
- Cold working can influence corrosion rates.

Intergranular corrosion is a localized attack at and adjacent to grain boundaries, with little corrosion in the grains. The alloy loses its strength and often disintegrates when exposed to a corrosive environment.

The major causes are:

- Segregation of impurities at grain boundary (Iron in aluminium alloys).
- Depletion of an alloying element in the area of grain boundary.

In stainless steels and nickel based alloys, intergranular corrosion is prevalent.
When exposed to a temperature in the range of 425 – 815°C (sensitization), Chromium Carbide (Cr$_{23}$C$_6$) precipitates at grain boundary leading to depletion of this corrosion-resistant element in the alloy. The role of chromium addition (upto 18%) to protect steels by inducing passivity is discussed already.

Microphotographs for unsensitized and sensitized stainless steels are shown in Fig. 38.1.

Chromium depletion as above induces corrosion in the grain boundaries, compared to surrounding grains. Decrease in chromium content in stainless steels increases critical passivating current densities and substantially restricting passive region stability. Below 12% Cr, the passive potential region is severely constricted. Percent carbon in the stainless steel influences sensitization time (higher the carbon, lower the time period to get sensitized). Nickel increases the activity of carbon in solid solution, facilitating carbide precipitation and enhancing sensitization.

Titanium or niobium carbides can prevent sensitization.

Sensitization of austenitic stainless steels during welding is termed WELD DECAY (see Fig. 38.2).
**Knifeline attack** is a localized form of intergranular corrosion occurring only a few grain diameters nearer to the weld zone in austenitic stainless steels.

![Diagram of weld decay in stainless steel](image)

The following treatments are recommended for abatement of intergranular attack of stainless steels.

- Solution annealing – Heating above $815^\circ$C to dissolve the precipitated chromium, followed by rapid cooling.
- Lower the carbon content (preferably below 0.03%).
- Addition of niobium or titanium for stabilization.

Some recommended tests for intergranular corrosion of stainless steels are given in Table 38.1.
Intergranular corrosion can occur in other alloys as well.

Ni – Cr alloys: Containing Cr, Mo and Fe - precipitation of moly – carbides at grain boundaries.

Aluminium alloys.

Al – Mg - \( \text{Mg}_2 \text{Al}_8 \) is anodic to matrix and initiates corrosion selectively at grain boundary.

Weldment corrosion is a serious problem. Drastic heating, melting, cooling cycles affects metallurgical and mechanical stability of the alloy.

Residual stresses and stress concentrations promote susceptibility to corrosion.

Weld metal composition need be so adjusted that the corrosion potential is shifted to nobler values.
When an alloying element is more active than the other in an alloy, selective dissolution leading to **dealloying** would occur in a corrosive environment.

Examples of dezincification of brasses and graphitic corrosion in grey cast-iron have been outlined already.

Other examples are illustrated below:

- Aluminium bronzes in acid chloride, HF - dealuminification.
- Tin bronzes in hot brine or steam – destannification.
- Cupronickels in refinery condenser tubes - Denickelification

Low-Zinc red brass (<15% Zn) is immune to dealloying. Tin additions to $\alpha + \beta$ castings accord good resistance. In single phase $\alpha$ admiralty brasses, small additions of As or Sb will be beneficial.

Effect of potentials in chloride electrolytes for copper and zinc separation from $\alpha$ – brass has been reported. Below about 0 – 0.1V, slow zinc oridation begins and at potentials below -0.8 – 0.9V, selective zinc dissolution occur. Above 0.0V, copper dissolves with formation of chlorides along with dezinfication. Between 0.0 to + 0.2V, redeposition of Cu$^{++}$ can occur. At more noble potentials, dissolution of copper and zinc increases.

Mg, Cu, Zn and Si are the most generally used alloying elements for aluminium.

Aluminium is active and readily oxidized to form protective oxide films on the surface.

These surface films are stable in aqueous solutions of pH 4.5 – 8.5, but not in strong alkali and acid solutions.
Coating of oxide film through conversion coating or anodising.

Galvanic corrosion of aluminium and alloys depends on the nature of the oxide film which influences its polarization and resistance.

Aluminium solid solution, microconstituents such as silicon and compounds such as $\text{Al}_2\text{Cu Mg}$ and $\text{Mg}_2\text{Si}$ exhibit varying electrode potentials and can form concentration cells within the alloy matrix.

Al – Mg alloys are relatively resistant to corrosion.

Al – Zn alloys used as galvanic anodes for protection of steel in marine environments.

Constituents in the matrix induce nonuniform attack. Localised corrosion such as pitting and intergranular attack is common.

Eg: Fe, Si, $\text{Al}_6\text{Mn}$, $\text{Mg}_2\text{Si}$, and $\text{Al}_3\text{Fe}$ impurities promote electrochemical corrosion.

Ageing and tempering heat treatments influence their corrosion behavior. Residual stresses can be introduced through thermomechanical treatments inducing stress corrosion cracking. Mechanical treatments including welding introduce corrosion, and susceptibility in heat-affected zones. Stress corrosion cracking develops in the simultaneous presence of tensile stress in a corrosive environment.

Metallurgical factors influencing stress corrosion are:

- Grain boundaries anodic to grain – localised strains
- Matrix – precipitate composition
- Nature of dispersion of precipitates and solute concentration
- Hydrogen embrittlement – diffusion of hydrogen
- Adsorption of ions at crack interface.

Cyclic stressing in a corrosion medium results in corrosion fatigue. Corrosion pits act as centres for corrosion propagation. Creep fracture at high temperatures
normally gets started at grain boundaries. Enhanced creep resistance can be provided by reinforcement with short fibres and introducing very minute intermetallics such as Al₃Fe Ni or particles.

Hydrogen in steels reduces ductility resulting in premature failure. Only a small quantity of ppm of hydrogen required to embrittle steel. Basic mechanism involves stress at a crack tip, where hydrogen can adsorb. Adsorbed atomic hydrogen then can migrate towards regions of localised stress and weaken the metal bond.

\[ \text{H}_2 \rightarrow 2\text{H} \rightarrow \text{H}_2 \]

Sources of hydrogen: Steel making operations
- Processing
- Welding
- Storage or Containment
- Exposed environment

Adsorption of hydrogen lowers surface free energy leading to crack propagation.

Hydrogen diffusion into the metal-alloy can occur in different ways:

Cathodic treatment (plating, pickling, cathodic protection)

Hydrogen during casting / solidification

Hydrogen occluded can create micro-voids and develop high pressure sites (H₂ – blistering)

Cracks can be developed through both intergranular and transgranular paths. Generally, hydrogen cracking is more prevalent at room temperature and the tendency deceases with higher temperatures.

Best remedy for hydrogen embrittlement is minimization (or prevention, of possible) of hydrogen availability in the environment.
Iron pillar of Delhi – A metallurgical marvel for corrosion resistance.

The iron pillar at Delhi (Fig. 38.3) is called a rustless wonder since it has withstood corrosion for the last 1600 years. It has naturally attracted the attention of corrosion engineers who are still without any definite scientific clue to the extraordinary corrosion resistance exhibited by such an ancient metallurgical structure exposed to atmospheric conditions. Even modern metallurgists are unable to reproduce such a corrosion-resistant metallic object, considering the advanced technologies available for iron and steel production, as at present. It becomes pertinent to analyze the secret of corrosion resistance of the Delhi iron pillar in the light of available research publications.

![Iron Pillar](image.png)

Reported chemical analysis (percent) of the iron varies from report to report:

C  0.08 -0.90  
Si  0.004 – 0.05  
S  Trace to 0.008  
P  0.114 – 0.48  
Mn  Nil
Microprobe analysis in the near-surface regions revealed presence of 0.05% Cu, 0.05% Ni, and 0.07% Mn with no chromium.

With respect to micro-structural features, the iron pillar material possesses a non-uniform grain structure, showing irregularly distributed slag inclusions in the unetched condition. Etched microstructure revealed medium to coarse polyhedral ferrite grains with slip bands in some grains. Pearlite not present at surface regions was observed to increase towards the interior.

Absence of uniform pearlite distribution is attributed to segregation of phosphorous. Relatively high proportions of slag inclusions was characteristic of the iron pillar samples. Nouniform distribution of slag particles is indicative of the processing technique used in ancient periods of history, namely, solid state reduction of high grade iron ore with charcoal followed by hammering to remove part of liquid slag. Majority of phosphorous is in solid solution.

The ancient process of iron extraction resulted in the presence of fine slag particles along with unreduced ore in the microstructure of the iron pillar samples. The microstructure of the iron in the Delhi pillar is typical of wrought iron. The composition of the iron, presence of phosphorous and absence of sulfur, its slag–enveloped metal–grain structure and passivity enhancement in presence of slag particles are attributed as possible reasons for its corrosion resistance. The nature of the protective passive layer on the iron pillar has been ascertained and found to be composed of iron hydrogen phosphate hydrate in the crystalline form in addition to $\alpha$, $\gamma$, and $\delta$ - FeOOH and magnetite, all in amorphous form.
REFERENCES
