Corrosion
MM 454 IITB
by
Prof. Vijayshankar Dandapani
Prof. Smrutiranjan Parida

https://somphene.github.io/notes/

Notes
by
Som S. Phene

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When Corrosion Engineers don't work, the world rusts.

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This is an **incomplete draft**. Please send corrections, comments, pictures of bad drawings, etc. to somphene1@gmail.com.

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1 Lecture Jan 13

§1.1 References

- Mars Guy Fontana's Corrosion engineering [Fo05].
- Edward McCafferty's Introduction to corrosion science [Mc10]
- R Winston Revie and Herbert H. Uhling's Corrosion and corrosion control: an introduction to corrosionscience and engineering [Re08]
- Specific scientific reports will be cited throughout the chapters and can be found in the Bibliography (at the end of these notes).

§1.2 Course objectives

- Provide a basic understansding of corrosion phenomena.
- Provide tools to measure, analyze and predict the corrosion of materials.
- Provide corrosion prevention and remediation strategies.

§1.3 Introduction to Corrosion

> **Question 1.3.1.** What is Corrosion?

Corrosion is degradation of materials. Basic notions of electrolyte, cathodes and anodes can be used to explain corrosion in Stainless Steel, pitting corrosion and other forms of corrosion. Any big tangible structures like ships or buildings or bridges, you will find steel/copper. Even in small devices like mobiles, laptops there are copper wires for conducting networks. Car frames and aeroplanes made of Aluminium. What metals undergo corrosion. Examples of corrosion detection are: rust in automobiles, titanium in implants (corrodes over a long period of time).

§1.4 Why study corrosion

- Fire on an aircraft Airbus A330 engine (Manchester, 2013) because of fracture of blades via fatigue. A good overview of applications of alloys in automative and aerospace industries is provided in [Zh+18].
- Bhopal Gas Tragedy also caused due to corrosion. Runaway chemical reaction-starts initiation but doesn't stop, for instance in mobile phones sparks. High temperature and pressure. High levels of chloroform. Carbon steel went corrosion in acidic media at high temperature.
- India loses upto \$100 billion annually (according to Hind Zinc CEO Sunil Duggal) thats about 4-5 % of the GDP.

- Conservation of materials: Limited supply of materials in specific geographical locations. Wastage of energy and human effort. Service extension mitigates additional manufacturing.

- Development of corrosion resistant alloy oxides.

- A good account of how important and complex corrosion can be is given in Comsol Blogs Corrosion Resistance.

§1.5 Corrosion- Is it complex?

Various environments have various features unique to each of them. For instance- salts are available in Marine environment, Chloride anions from salts is significant. Sulphur dioxide in industrial applications. Sulphate anion in the soil. Materials prone to corrosion are steel, stainless steel, aluminium alloys, copper, nickel, titanium alloys. Complex systems of materials. Different case studies map to different root causes.

§1.6 Corrosion- An interdisciplinary field

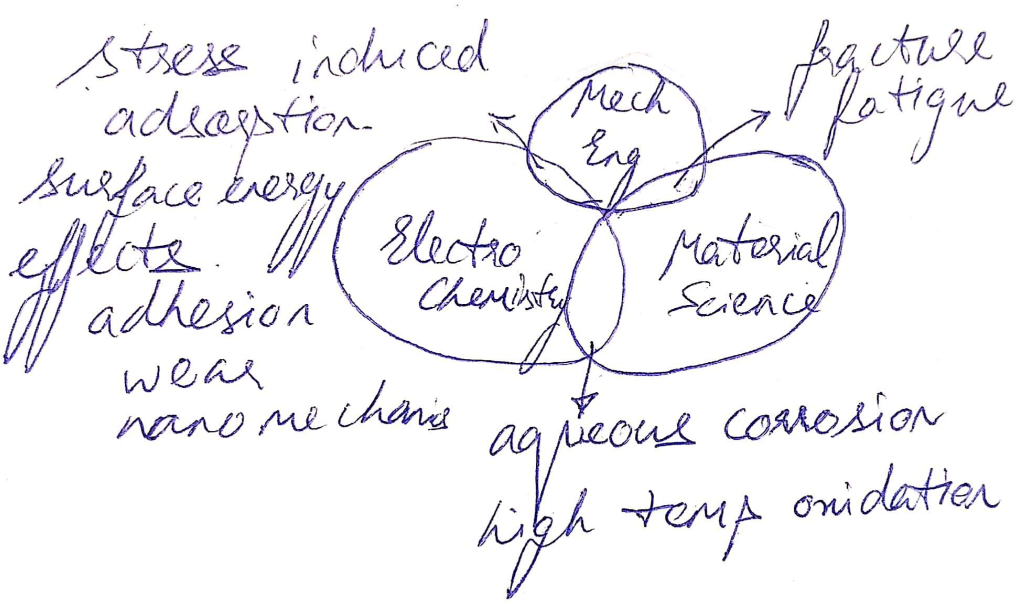
stress induced
adsorption
surface energy
effects
adhesion
wear
nano mechanics
Mech
Eng
fracture
fatigue
Electro
Chemistry
Material
Science
aqueous corrosion
high temp oxidation

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Figure 1.1: Venn Diagram of interacting fields

Electrochemistry, Mechanics/Engineering, Materials Science as in fig. 1.1. Involves interaction of Stress induced adsorption surface energy defects- adhesion, wear, nanomechanics, tribology. Aqueous corrosion- high temperature oxidation.

§1.7 Corrosion- Definition

Origin- comes from Latin corrodere- gnaw away or eat away.

Corrosion is characterized as:

- Natural phenomenon
- destructive attack on metal by its environment, mainly electrochemical factors.
- causes deterioration of properties of the metal.

Plastics, concrete, wood, ceramics, composite materials undergo deterioration by environment but don't corrode.
Rusting applies to plain carbon steel and iron. **Rust**: hydrated ferric oxide is red or dark brown color. Non ferrous metals- aluminium, copper, zinc corrode but don't rust.

§1.8 Thermodynamic viewpoint

Thermodynamic reaction by which a metal returns back to its natural form as an ore. Extraction/alloying is gaining energy (opposite to spontaneous reaction requires input of energy). Corrosion involves release of energy. This is in the opposite direction of extractive metallurgy.

For instance, $\mathrm{Fe} + C$ (+Cr, Ni, Si) corrosion cycle.

Fe alloys - Haematite (Fe_2O_3), Wustite (FeO) are common.

Cr_2O_3 layer stops corrosion. Thermodynamics drives corrosion.

§1.9 Electrochemical Reactions

Corrosion is predominantly an electrochemical process involving coupled electrochemical half cell reactions.

Half Cell reaction- Anodic

- Species undergoes oxidation.
- Loss of electrons from the species at the anodic site, ie. electrons are produced at the anodic site.

Example 1.9.1

The following reactions are common examples of anodic reactions:

- $\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2e^-$
- $Al \longrightarrow Al^{3+} + 3e^-$
- $2\mathrm{Cu}\,(s) + H_2O\,(l) \longrightarrow \mathrm{Cu}_2O\,(s) + 2H^+\,(aq) + 2e^-$

Half Cell reaction- Cathodic

- Species undergoes reduction.
- Gain of electrons for species at the cathodic site, ie. electrons are consumed at the cathode.

Example 1.9.2

The following reactions are common examples of anodic reactions:

- In acidic medium: $H^+ + 2e^- \longrightarrow H_2$
- In basic/neutral medium: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \,(aq)$

Charge + Mass transport.

Corrosion involves simultaneous transfer of mass and charge across a metal/solution interface.

Corrosion involves both half cell reactions to form a coupled electrochemical reaction.

Example 1.9.3 (Iron in Acidic Solution Environment)

The following half-cell reactions couple to give an electrochemical reaction for Iron corrosion in acidic environment as shown in fig. 1.2.

$$\begin{array}{rccc}
\text{At anodic sites:} & \mathrm{Fe} & \longrightarrow & \mathrm{Fe}^{2+} + 2e^- \\
\text{At cathodic sites:} & 2H^+ + 2e^- & \longrightarrow & H_2 \\
\hline
\text{Overall reaction:} & \mathrm{Fe} + 2H^+ & \longrightarrow & \mathrm{Fe}^{2+} + H_2
\end{array}$$

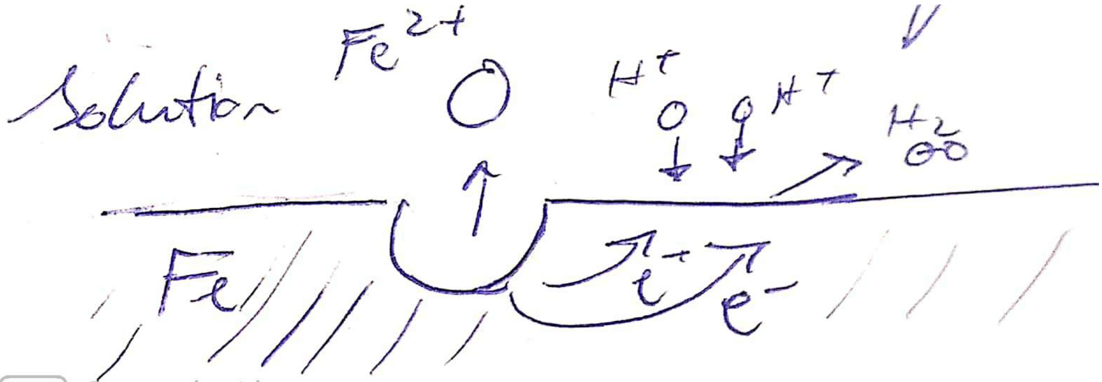

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Figure 1.2: Fe surface corroding in Acidic Medium

Thus, corrosion involves the following components:

- Anodic reaction

- Cathodic reaction
- Electrolyte
- Metallic contact to serve as path between anode and cathode for electron transport.

> **Question 1.9.4.** How can two different electrochemical reactions happen on the same metal surface?

Energy of surface drives reaction. Difference in energies between two points on the metal surfaces exist thus favoring different reactions at different points. Insert diagram (later). *Heterogeneous nature of the surface* creates difference in energy.

Example 1.9.5 (Iron Surface immersed in Neutral/Alkaline medium)

The following half-cell reactions couple to give an electrochemical reaction for Iron corrosion in neutral/alkaline environment as shown in **??**.

$$\begin{array}{cccc} \text{At anodic sites:} & 2[\mathrm{Fe}\ (\mathrm{s}) & \longrightarrow & \mathrm{Fe}^{2+}(\mathrm{aq}) + 2e^-\ ] \\ \text{At cathodic sites:} & O_2\,(g) + 2H_2O\,(l) + 4e^- & \longrightarrow & 4\mathrm{OH}^-\,(\mathrm{aq}) \\ \hline \text{Overall reaction:} & 2\mathrm{Fe}\,(s) + O_2\,(g) + 2H_2O\,(l) & \longrightarrow & 2\mathrm{Fe}^{2+}(\mathrm{aq}) + 4\mathrm{OH}^-\,(\mathrm{aq}) \end{array}$$

The aqueous species formed may further react as

$$\mathrm{Fe}^{2+}(aq) + 2\mathrm{OH}^-(aq) \to \mathrm{Fe}(OH)_2\,(s)$$

This leads to precipitation of ferrous hydroxide on the Iron surface. In the presence of water, this forms hydrated ferric oxide as

$$2\mathrm{Fe}(OH)_2\,(s) + (x-1)H_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O\,(s) + 2H^+\,(\mathrm{aq}) + 2e^-$$

> **Remark 1.9.6** — In the presence of an acidic media, there was a different reaction leading to Hydrogen embrittlement.

§1.10 Faraday's Law

Corrosion involves simultaneous charge and mass transfer. Charge transfer and Mass transfer related by **Faraday's Law** which states that the mass W of metal (liberated or deposited/corroded) is given by:

$$W = \frac{ItM}{nF} \tag{1.1}$$

where F is called the **Faraday's Constant**.

$$F = \frac{96500\,C}{\text{Mole equivalent}}$$

I is the current, t is the time taken for the transfer, M is the Molar Mass of the metal and n is the # of elementary charge (e) particles per mole of the metal involved in the reaction given by the stoichiometry.

Example 1.10.1 (Iron half cell reaction)

Consider the Reaction:

$$\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2e^-$$

This involves 2 e^- per mole of Fe^{2+} produced. Thus, $n = 2$ is to be used in Faraday's Law.

2 Lecture Feb 3

Quiz 1 on Monday, 10th Feb.

§2.1 Pourbaix Diagram

Last time we constructed the Pourbaix Diagram of Al. If the equation involves both the H^+ and e^-, then the pH is related to the Voltage.
We also related the Corrosion tendency to the regions in the Pourbaix Diagram. In very high and very low pH values, we see the phases favored are in line with corrosion. It doesn't give rate of corrosion. Seaparate plot for rate of corrosion. In this case it matches the thermodynamics plot closely. However, kinetics and thermodynamics may not correlate in general.

§2.2 Pourbaix Diagram of Water

Line a: Cathodic evolution of hydrogen

$$\begin{aligned} 2H^+ + 2e^- &\longrightarrow H_2 \quad &&: \text{cathodic evolution of } H_2 \text{ (acidic media)} \\ 2H_2O + 2e^- &\longrightarrow 2OH^- + H_2 \quad &&: \text{basic media} \end{aligned}$$

Note that both reactions above are equivalent, just expressed in terms of acidic or basic constituents depending on the environment. If we have the reaction, we would have from the Nernst equation:

$$E = 0.000 - 0.0591\text{pH}$$

Compare this with the previous Al Pourbaix diagram, the reduced species is stable below the line. Should be able to predict which species is stable below and below the lines.
Line b: Anodic evolution of O_2

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

If we have the reaction, we would have from the Nernst equation:

$$\begin{aligned} E &= E^0 - \frac{2.3030RT}{nF}\log\frac{1}{H^{+4}} \\ E &= 1.228 - 0.059\,\text{pH} \end{aligned}$$

Here also the reduced species that is H_2O, is stable below the line b, whereas oxidized species O_2 is stable above the line b.
In Zinc diagram, below loine a, H_2 is stable so the counter reaction to $Zn \to Zn^{2+}$ is given by cathodic reaction Hydrogen evolution as $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$. In the middle region where ZnO is formed, it is the passive layer and hence corrosion is prevented. ZnO is also called white rust.
Above the line a, and below line b, we have Water to be stable. Hence, oxygen gets reduced to produce water (green box).
Above line b, we don't have oxygen reduction or hydrogen evolution. We need a very strong oxidizing agent such as sulphuric acid or nitric acid.

§2.3 Pourbaix Diagram of Iron

> **Question 2.3.1.** How to protect Iron?

Couple Iron with Zinc to provide **cathodic protection**. That is Zn oxidizes ans Fe is protected as the cathode.
Forming passive iron oxide also good: called **anodic protection**.
We could also increase the pH to reach the passive zone.

§2.4 Pourbaix Diagram for Stainless Steel

Chromium provides resistance.

§2.5 Pourbaix diagram for Gold

No oxidation of Gold below line a, or b. Au is stable above up to change of phase to Au$(OH)_3$. At high potentials, above line b, there can be Oxygen evolution by reduction of Au^{3+}.

§2.5.i Pourbaix Diagram of Cu

Hydrogen evolution cannot take place with Copper.

> **Question 2.5.1.** Will Copper corrode in Deaerated acid?

No O_2 present. Only H^+ present which cannot take place to oxidize Cu. Hence not possible.

> **Question 2.5.2.** Why do we use Cu in pipes. Tendency to corrode not same as kinetics.

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