Overvew of Corrosion Science, Engineering and Technology

Citation for published version (APA):
Lyon, S. B., & Feron, D. (Ed.) (2012). Overvew of Corrosion Science, Engineering and Technology. In *Nuclear Corrosion Science and Engineering* Woodhead Publishing.

Published in:
Nuclear Corrosion Science and Engineering

Chapter 1: Overview of Corrosion Science

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1.1 Introduction

Corrosion engineering, science and technology is the study of the interaction of materials with the environment in which they are used. Corrosion requires a comprehensive multidisciplinary and interdisciplinary outlook with core knowledge from the fields of metallurgy/materials science together with electrochemistry/surface science. Other important disciplines of relevance include: chemical engineering (particularly fluid flow), chemistry and geochemistry, conservation science, mechanical engineering and structural integrity. This chapter is intended to comprise a brief introduction to the science and technology of aqueous corrosion with an emphasis on fundamental theory. It is not intended to provide a comprehensive treatment of the subject since there are many textbooks that undertake this task to much greater depth than is possible here.

1.1.1 Definition of corrosion

Corrosion is strictly the <u>process</u> that results in the deterioration of the performance of a material the result of which is corrosion <u>damage</u>. Corrosion may be defined as: "a physico-chemical interaction leading to a significant deterioration of the functional properties of either a material, or the environment with which it has interacted, or both of these" [1]. It is important to note that although "corrosion" is more commonly understood to involve electrochemical deterioration, such as metal dissolution, the ISO standard definition (above) also encompasses the deterioration of non-metals. The definition includes processes that involve combinations of environmental (i.e. chemical and/or electrochemical) deterioration where these are additionally influenced by applied or residual stresses in the material, and by the material microstructure as a result of manufacture or service. However materials degradation arising from mechanisms that do not involve environmental interaction, for example mechanical overstressing, or degradation of polymers under ultraviolet radiation, fall outside this definition of corrosion.

1.1.2 Corrosion environments

Corrosion damage to materials can be caused by a wide variety of environments. More specifically it is combinations of material and environment that gives rise to corrosion damage. The most widely understood situation is for metallic (electrochemical) corrosion in aqueous (i.e. water-containing) environments with or without dissolved species such as electrolytes (i.e. salts) and reactants (e.g. dissolved oxygen). However, corrosion damage also results from other material-environment combinations: e.g. solvent cracking of polymeric materials, "bleeding" corrosion of aluminium in chlorinated hydrocarbons and sulphate attack on cementitious materials such as concrete. Corrosion damage also results from exposure of materials to gaseous atmospheres, such as air, steam, etc (e.g. high-temperature corrosion).

1.1.3 Examples of corrosion damage

General or uniform corrosion, where active metal dissolution is the dominant corrosion mechanism, is not normally of great significance in nuclear plant as corrosion resistant (passive) alloys (e.g. stainless steels, nickel alloys, zirconium fuel cladding) are the workhorse materials that in use. However, general corrosion may also be of significance in the civil engineering structures associated with the nuclear site. Importantly general corrosion is the main controlling mechanism for certain materials used in nuclear waste containment (e.g. copper, carbon steels, cast iron, etc.)

Localised forms of corrosion (i.e. pitting, intergranular attack, stress corrosion cracking, or corrosion fatigue) are generally more important and are often critical to reactor plant performance and lifetime. Similarly the lifetime of nuclear waste containers manufactured from corrosion-resistant alloys is dependent upon localised corrosion damage, Figure 1. As another example, corrosion processes that are associated with flow of fluids within the plant, can give rise to flow-assisted corrosion, Figure 2.

Figure 1: Surface stress corrosion cracks initiating from a pit in 316L stainless steel exposed to a MgCl$_2$ salt deposit at a relative humidity of 30% and at 40°C.

Figure 2: Flow-assisted corrosion (erosion-corrosion) on seawater-cooled copper condenser tubing from 500MW coal-fired station

1.1.4 Economics of corrosion

Although difficult to quantify, the cost of corrosion in developed economies is often estimated to be in the range 2-4% of Gross National Product per annum [2]. Generally the costs of material, manufacture, installation and commissioning, etc., are included in this amount. However, it is often the costs of service failures (i.e. repairs and especially lost production) that are the most significant and the most difficult to quantify. For existing nuclear plant, the safety cases for life extension are often predicated on continuing good corrosion performance

of the service components, including the reactor pressure vessel. For new build plant, the challenges of achieving 60 year life are formidable and understanding the key corrosion mechanisms (and how to control or limit corrosion damage) is critical to developing reliable systems [3].

1.2 Fundamentals of aqueous metallic corrosion

1.2.1 Electrochemistry

The overall corrosion process <u>necessarily</u> involves at least two simultaneous reactions: an oxidation (or anodic) reaction and a reduction (or cathodic reaction), which are coupled through the exchange of electrons and are therefore known as electrochemical reactions. Examples of anodic (oxidation, electron-donating) reactions include:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(metal dissolution)} \qquad \textbf{... (1)}$$
$$Cr + 3H_2O \rightarrow Cr(OH)_3 + 3H^+ + 3e^- \quad \text{(passivity)} \qquad \textbf{... (2)}$$
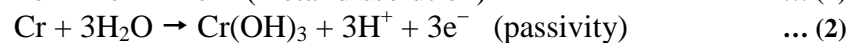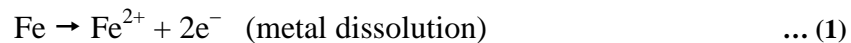
While examples of cathodic (reduction, electron-accepting) reactions include:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(oxygen reduction)} \qquad \textbf{... (3)}$$
$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(hydrogen evolution)} \qquad \textbf{... (4)}$$

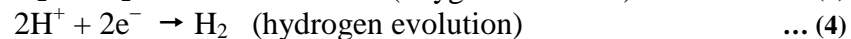A corrosion cell, therefore, necessarily contains an anode, a cathode and an electrolyte (i.e. a medium through which the ionic species involved in the anodic and cathodic reactions are transported). For aqueous corrosion the electrolyte also contains the corrosive medium or agents and contains dissolved products of corrosion (e.g. ions, colloids and neutral species).

It is important to appreciate that a corrosion cell involves two simultaneous reactions (anodic and cathodic) that <u>must</u> proceed at the same time and the same rate, but not in the same place. Thus, anodes and cathodes are necessarily spatially separated.

1.2.2 Anode and cathode separation

During corrosion, the local electrochemical potential (or voltage) at an anode is different from that at a cathode. Also, the local electrochemical reactions at anodes and cathodes result in significant chemical changes in their vicinity that encourage and maintain their spatial separation. Furthermore, this potential difference in solution gives rise to a voltage gradient, which attracts oppositely charged ions (or repels similarly charged ions) a process known as electro-migration. Additionally, the requirement for electro-neutrality in the electrolyte (by which is meant that an anion cannot exist in solution without a corresponding cation) gives rise to diffusion in the electrolyte. The overall process for corrosion of iron, with oxygen as the cathodic reactant, is shown schematically in Figure 3, with migration and diffusion of ions carrying the flow of current.
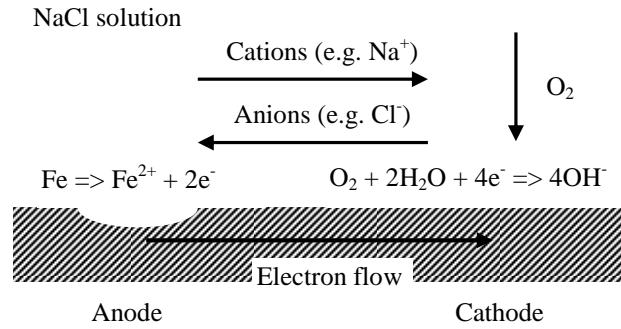
**Figure 3: Schematic diagram showing spatial separation of anode from cathode
with corresponding migration of ions in solution.**

It is important to note that corrosion damage (e.g. metal loss) generally occurs at the anodic locations while at the cathodic locations no corrosion damage occurs. For alloys subject to general corrosion, the locations of anodes and cathodes tend to move randomly over the surface of the metal and, on average, metal thinning occurs relatively uniformly. However, for corrosion resistant alloys, which are covered by a passive oxide film, the location of an anode tends to become strongly localised thus giving rise to localised corrosion damage: e.g. pitting corrosion, crevice corrosion and stress-corrosion cracking.

1.2.3 Electrochemical thermodynamics

The controlling thermodynamic equation for an electrochemical process is the Nernst equation that relates the equilibrium constant, K, for a reaction:

$$\text{reactants} \rightleftharpoons \text{products} \quad : \quad K = \frac{\prod a(\text{products})}{\prod a(\text{reactants})} \qquad \dots (5)$$

Where the mathematical operator symbol $\prod$ means "the product of", and $a(x)$ means "the thermodynamic activity of species x". Thus, for the copper plating (displacement) reaction on iron:

$$Cu^{2+} + Fe \rightleftharpoons Cu + Fe^{2+} \qquad \dots (6)$$

$$K = \frac{a(Fe^{2+}) \times a(Cu)}{a(Cu^{2+}) \times a(Fe)} \approx \frac{[Fe^{2+}]}{[Cu^{2+}]} \qquad \dots (7)$$

By convention, the activity of a pure substance in its standard state (i.e. pure copper, Cu, and iron, Fe) is equal to 1; also, the activity of a substance is approximately equal to its concentration, except at high concentrations (typically $\gg 0.5$ M). Thus, $a(x) \approx [x]$ where the square brackets means "the concentration of the species x" and the equation for the equilibrium constant may be approximated as indicated above.

The Gibbs Free Energy (ΔG) for a reaction is defined as:

$$\Delta G = -RT \ln(K) = -zFE \qquad \dots (8)$$

Where: R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), $\ln(K)$ is the natural logarithm of the equilibrium constant for the reaction, F is Faraday's constant (96,485 C mol^{-1}), z is the amount of charge (number of electrons) passed in the electrochemical reaction and E is the electrode potential for the reaction (V).

Note that the electrode potential for an electrochemical reaction is a thermodynamic quantity that is simply related to the free energy change in the system for that reaction. Also, due to the relation between the free energy and the equilibrium constant, the electrode potential for a reaction can be predicted from a knowledge of the concentrations (or activities) of the species present via the Nernst equation:

$$E_o = \frac{-RT}{zF}\ln(K) \qquad\qquad \textbf{... (9)}$$

One important consideration arises from the practical requirement of measuring a potential difference; thus a single potential cannot be measured in isolation. By convention, the hydrogen electrode is taken to be the primary standard to which all other potentials are referred:

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad\qquad \textbf{... (10)}$$

The potential of the standard hydrogen electrode at a hydrogen gas pressure of 1 bar, a hydrogen ion activity[1] equal to 1 and at 298 K has, by convention, an electrochemical potential of 0 V. Potentials measured with respect to the hydrogen electrode are known as on the Standard Hydrogen Electrode (SHE) scale. Since the hydrogen electrode is inconvenient to use, other secondary reference electrodes are in common use, for example the saturated calomel electrode (SCE): i.e. mercury/mercury chloride in saturated potassium chloride solution.

1.2.4 Passivity

The phenomenon of passivity was probably first recorded by James Keir in 1790 on the exposure of iron to concentrated nitric acid [4] and later famously studied by Michael Faraday in 1836 [5]. Passivity is now understood to be caused by the solid-state electrochemical oxidation of a metallic substrate, under the correct conditions of potential and pH, to a solid species that is largely stable to dissolution. Thus, on formation of a compact and continuous film on a metal surface, the kinetic processes involved in corrosion (e.g. electron and ion charge transfer, diffusion of reacting species, etc.) are slowed by many orders of magnitude. For many alloys passivity occurs at intermediate pH and at sufficiently high oxidising potentials and most commonly (though not exclusively) results in the formation of an oxide film. The literature on passivity in general is extensive and of interest are the mechanisms of passive oxide film formation, its structure and composition, the long-term stability of the film and its local breakdown in the presence of species such as chloride ions and others (i.e. pitting).

For iron, the passive oxide is thermodynamically stable at sufficiently high potentials and is chemically stable to dissolution except in strong acid and alkali. However, it is unstable to cathodic reduction both to a ferrous species and directly to the metal. This is fundamentally

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[1] Note that this is not the same as a solution containing 1 mole of hydrogen ions (e.g. 1 M hydrochloric acid) because, in relatively concentrated solutions, the activity of an ion is affected by the concentration of both itself and of other ions. Thus, an HCl solution where the hydrogen ion activity equals 1 is approximately 1.18 Molar.

different behaviour to many other common passive systems (e.g. chromium-containing alloys) where the passive oxides formed are generally stable to reduction.

In the strict sense, passivity relates to the process of oxidation leading to a solid corrosion product that forms in such a way (i.e. thermodynamically, or at least kinetically, stable, continuous, without substantive defects, relatively insoluble and generally resistant to further oxidation or reduction) as to provide a significantly protective film. Thus, although passive oxide films are by far the most important type, passive films may also consist of other chemistries such as sulphides, chlorides, etc. For example, in sulphide environments, steel may passivate with an iron sulphide film while in chloride environments lead will passivate by the formation of insoluble lead chloride film.

Other forms of corrosion that result in the formation of surface films with significant protective properties are often the result not of direct oxidation to a solid species, but rather by precipitation of an insoluble salt that covers the metal surface, e.g. iron phosphate. In the strict sense, this is not "passivity", although it is often described as such particularly if the end result (a greatly reduced corrosion rate and a tendency for corrosion to occur in a localised manner) is similar. In some cases, however, it is unclear whether the film forms by direct oxidation or by precipitation. For example, a protective ferrous sulphate "salt film" forms during corrosion of steel in concentrated sulphuric acid [6], since iron sulphate is relatively insoluble in this environment.

1.2.5 Pourbaix diagrams

The acidity or alkalinity of an environment fundamentally affects the extent of corrosion damage and, hence, the pH (or negative logarithm of the hydrogen ion concentration) is of significant importance in predicting corrosion processes. In corrosion science, maps of potential v. pH are known as Pourbaix diagrams after their originator; more commonly they are known as E_H v. pH diagrams. The usefulness of a Pourbaix diagram is shown below where domains of stability for various dissolved species as a function of potential and pH are shown. This offers a method for predicting the nature of the surface of the material under a given set of environmental and electrochemical conditions. Thus, at 298K and a potential of 0V (SHE) iron is predicted to dissolve, (i.e. the stable species is Fe^{2+}) at pH < 7, while it passivates (i.e. the stable species is FeO(OH)) at pH > 7, Figure 4. Pourbaix diagrams may be drawn at arbitrary temperature and pressure provided that a liquid aqueous phase exists to solvate the ions present in the liquid environment. Similar diagrams may be drawn for nickel, Figure 5, chromium, Figure 6 and for austenitic stainless steel (i.e. iron+nickel+chromium), Figure 7.
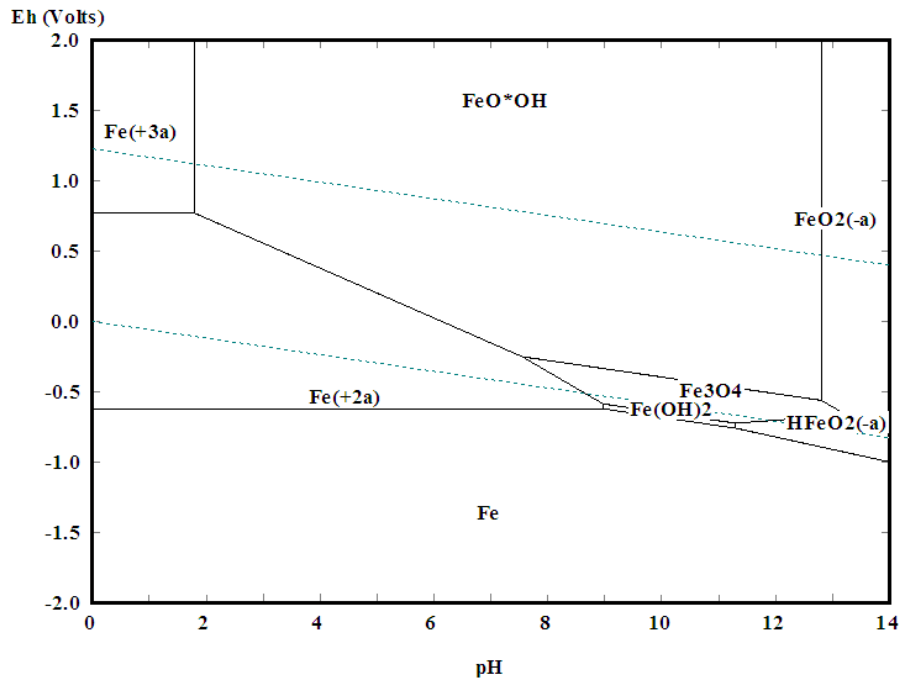
Figure 4: Pourbaix diagram for iron at 298 K with soluble species at concentration of 10^{-5} M and with the most common stable oxide species present [7]
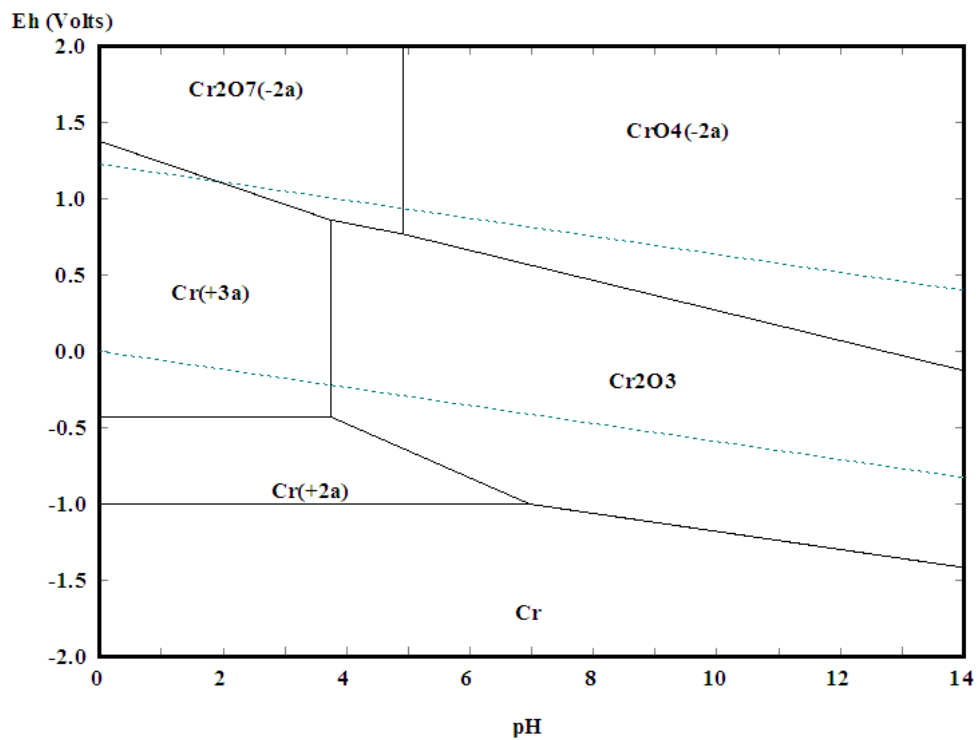
Figure 5: Pourbaix diagram for chromium at 298 K with soluble species at concentration of 10^{-5} M and with the most common stable oxide species present [7]
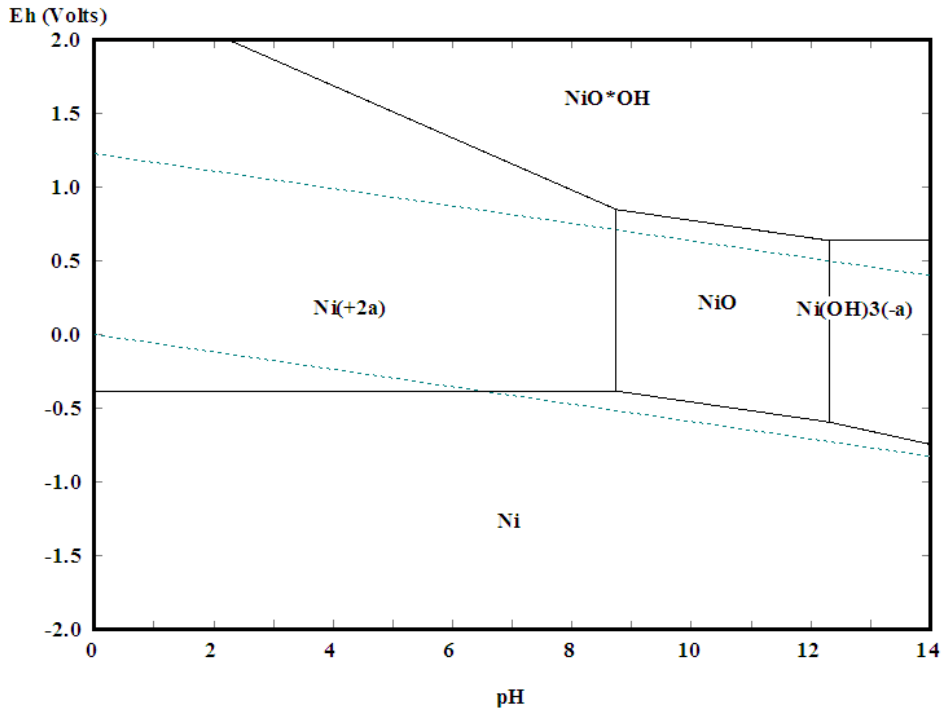
Figure 6: Pourbaix diagram for nickel at 298K with soluble species at concentration of 10^{-5} M and with the most common stable oxide species present [7]
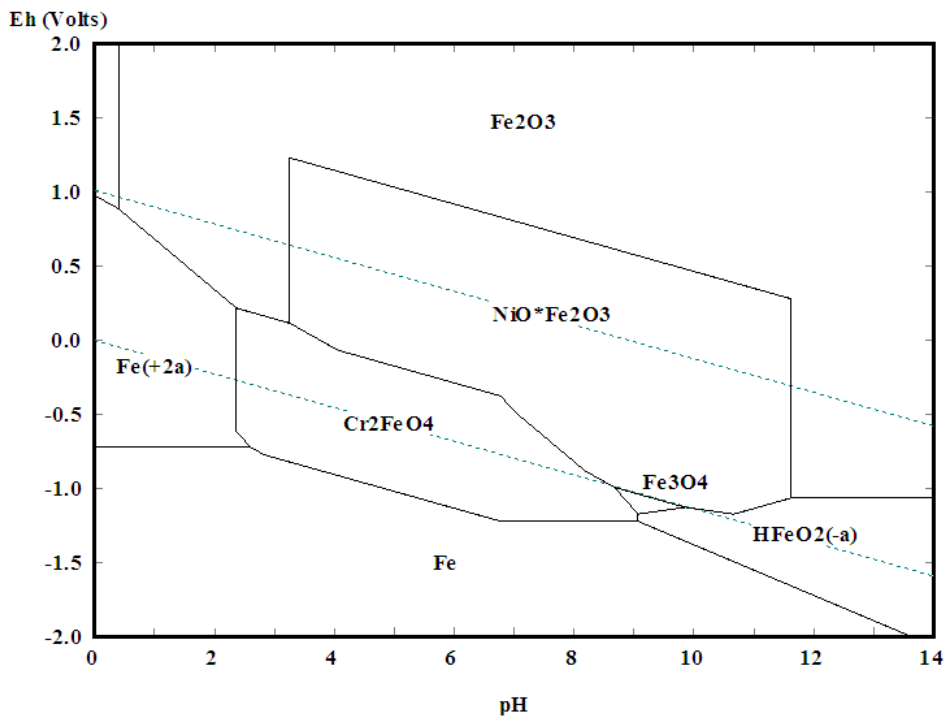
Figure 7: Pourbaix diagram for iron, chromium, nickel (i.e. austenitic stainless steel) at 573K (300°C) with soluble iron, chromium and nickel species at concentration of 10^{-5} M and with the most common stable oxide species present [7]

1.2.6 Electrochemical kinetics

The rate of an electrochemical corrosion reaction may be, in principle, be determined by measuring the current that flows between all the anodes and all the cathodes. The mass loss of

the metal is then obtained by the application of Faraday's Law, which relates the current flowing to the mass of material corroded (or deposited in the inverse situation):

$$\text{Mass loss} = \frac{I \times t \times M}{z \times F} \qquad \text{... (11)}$$

Where: I is the current flowing, t is the time the current flows (i.e. $I \times t$ is the charge passed), M is the molar mass of the material, z is the number of electrons involved in the reaction and F is Faraday's constant. A more useful measure of corrosion rate is the mass loss per unit area of metal (rather than total mass lost) and this is easily determined by replacing the total current (I) in the above equation by the current per unit area (i.e. current density, i).

Unfortunately, for the self-corrosion of a metal, the anodes and cathodes are effectively short-circuited via the metallic (electron-conducting) substrate and the anode-to-cathode current cannot be easily measured. However, where the electrochemical elements (i.e. anode and cathode) can be clearly separated (e.g. in a galvanic cell) then it is possible to measure the current conventionally. Where the electrochemical elements are closely spaced on the metal and, hence, cannot be easily separated, measurement of the current flowing in the electrolyte can provide an indirect measure of the overall anode-to-cathode current.

When the electrode reaction is controlled by electrical charge transfer at the electrode (and not by mass transfer) then the governing relationship between current and potential is the Butler-Volmer equation, which can be derived from activation state theory:

$$I = \text{rate of forward reaction} - \text{rate of reverse reaction} \qquad \text{... (12)}$$

$$I = A.i_o \left\{ \exp\left[\frac{(1-\alpha)z.F}{R.T}(E - E_{eq.}) \right] - \exp\left[-\frac{\alpha.z.F}{R.T}(E - E_{eq.}) \right] \right\} \qquad \text{... (13)}$$

Where, I is the current flowing, A is the area of the reacting metal (electrode area), i_o is the rate of the forward and reverse reactions at equilibrium (known as the exchange current density), z is the number of electrons in the reaction, E is the electrode potential, $E_{eq.}$ is the electrode potential at equilibrium, R is the gas constant, T is the absolute temperature and α is the "shape factor" for the reaction (commonly taken to equal 0.5). The term $(E - E_{eq.})$ is sometimes known as the overpotential (η).

The Butler-Volmer equation has two limiting cases. Firstly, in the high overpotential regime where $(E - E_{eq.})$ is large (> 50 mV), the equation simplifies to the Tafel equation:

$$\eta = a - b \log(|i|) \qquad \text{... (14)}$$

Where, η is the overpotential, a and b are constants that depend on the nature of the anodic and cathodic reactions, and $|i|$ is the absolute value of the current density. The term b is often known as the Tafel slope. Secondly, in the low potential regime where $(E - E_{eq.})$ is small (< 10 mV), then the current-potential relationship becomes linear:

$$\eta = \frac{RT}{nF} \cdot \frac{i}{i_o} \qquad \text{... (15)}$$

In the low potential regime an expression for the polarisation resistance, R_p, may be derived (also known as the Stern-Geary relationship):

$$\frac{\Delta E}{\Delta I} = R_p = \frac{b_a.b_c}{2.3(b_a + b_c)}.\frac{1}{i_{corr}} \qquad \text{... (16)}$$

Where, ΔE and ΔI are, respectively, the changes in applied voltage and current, b_a and b_c are, respectively, the anodic and cathodic Tafel slopes and i_{corr} is the corrosion current. This gives a method for the measurement of corrosion rate (from the corrosion current density) by measurement of the polarisation resistance.

The polarisation resistance, which is a consequence of an activation-controlled electro-chemical process such as metal dissolution, must not be confused with the ohmic resistance given by Ohm's law, which has the same mathematical form (i.e. potential is proportional to current):

$$V = I.R \qquad \text{... (17)}$$

Where, for a conductor, the potential difference, V across a conductor with current, I, flowing through it is proportional to the ohmic resistance, R. Generally ohmic resistance is only of concern in electrochemistry where the conductivity of the electrolyte is low (i.e. the resistance is large) or the current is large.

As the rate of reaction increases (i.e. the anode-to-cathode current increases) the rate of arrival of the reacting species at the electrochemical interface (e.g. the reacting metal) will become limited by the rate of diffusion of the reacting species in the electrolyte. Thus, as the current increases, the interfacial concentration of the reacting species at the electrode decreases and, when it reaches zero, there can be no further driving force for mass transport in solution, which, therefore, becomes controlled by diffusion processes in solution, Figure 8. At this diffusion limit, Fick's 1st Law holds and the limiting current is:

$$I_{lim} = D.F.z/\delta$$

Where: I_{lim} is the diffusion limited current, D is the diffusion coefficient of the reacting species, F is Faraday's constant, z is the number of electrons transferred in the reaction and δ s the diffusion distance (or stagnant boundary layer).
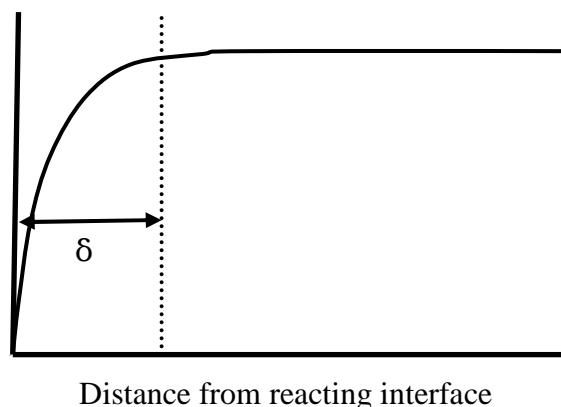

Distance from reacting interface

1.2.7 Mass transport

For many technically important applications the corrosion rate is controlled by the diffusion of the reacting species to the metal surface and/or the diffusion of dissolved species away from the surface. Under these conditions, mass transport in the solution becomes critical. In general mass transport occurs by three fundamental processes:

- Diffusion (i.e. movement under a concentration gradient)
- Migration (i.e. movement under an electric field gradient)
- Convection (i.e. natural or forced solution flow)

The total flux of reactant to a surface or interface (i.e. the total mass transport) is obtained simply by addition of the components of diffusion and migration to that of convection:

$$\text{Total Flux} = \text{Diffusional Flux} + \text{Migrational Flux} + \text{Convective Flux} \quad \text{... (18)}$$

In all flow conditions a region of fluid exists adjacent to the surface of the electrode in which no convection occurs, only diffusion and migration; this is called the boundary layer and may be equated with the diffusion distance in Fick's Law. Generally, as the convection rate increases the boundary layer is compressed and reduced in extent and, hence, the overall rate of mass transport increases.

General corrosion proceeds commonly under mass-transport controlled conditions where the above situation applies and therefore an increase in the fluid flow rate will increase the corrosion rate. However, for passive alloys subject to localised corrosion, an increase in the fluid flow rate often results in a decrease in the localised corrosion rate. This is because chemical heterogeneities that are crucial for the development of a localised cell are more easily disturbed at high flow rate. This is one of the reasons why components should not be left containing stagnant fluids for extended periods of time otherwise the localised corrosion risk increases and pitting corrosion, for example, can initiate.

1.2.8 Effect of flow rate on corrosion

For corroding systems, under mass transport control, the flux of species to a surface where the rate-controlling reaction is occurring is described in the steady-state by Fick's 1st Law. This flux may be also measured electrochemically by the limiting current for that reaction (e.g. oxygen reduction). In this way, a mass transfer coefficient, k, may be defined by:

$$k = \frac{i_{\text{lim}}}{zFC_b} \quad \text{... (19)}$$

Where: i_{lim} is the limiting current density for a cathodic reaction, C_b is the bulk concentration of cathodic reactant, F is Faraday's constant and z is the number of electrons (i.e. units of charge) transferred in the reaction. For a corrosion process whose rate is controlled by mass transfer of cathodic reactant, for example carbon steel in neutral, oxygen-containing solutions, knowledge of the mass transfer coefficient, k, enables prediction of corrosion rate.

Measurement of the diffusion flux may be carried out using standard electrochemical techniques as a function of fluid flow rate, either via rotating electrode systems, or via

electrodes placed in flow channels. For laminar flow the analytical solution predicts that the limiting current (i_{lim}) at a rotating electrode is proportional to the concentration of reacting species in solution and the square root of the rotation speed, the Levich equation [8]:

$$i_{lim} = A \ C \ \omega^{0.5} \qquad\qquad \text{... (20)}$$

Where: ω is the angular rotation rate of the electrode (radians s^{-1}), C is the concentration of reacting species and A is a constant that depends on the fluid properties and diffusion rate of the reacting species. Thus, if a plot of i_{lim} v. $\omega^{0.5}$ is a straight line, then the reaction is mass-transport controlled and the diffusion coefficient for the reacting species can be obtained from the slope of the straight line.

For turbulent flow, the situation is more complex and cannot be solved analytically hence experimental analogies for particular situations must be developed. Nevertheless, similar results hold overall in that the limiting current at an electrode is proportional to the fluid flow rate to some power. For flow in smooth-bored pipes, which is of relevance in a great number of situations, the experimentally derived result is of the form:

$$k = A \ v^n \qquad\qquad \text{... (21)}$$

Where A is a constant dependent on the fluid properties, v is the fluid flow rate and n an exponent that lies generally between 0.5 and 0.8.

1.2.9 Radiolysis of water

In an aqueous environment ionising radiation will cause the formation of a number of intermediate species that have relatively short lifetimes. These include radicals (e.g. free electrons, hydrogen, hydroxyl, etc.), gases (e.g. hydrogen, oxygen, etc.), neutral species (e.g. hydrogen peroxide, etc.) and ions (e.g. protons, hydroxide, etc.). During radiolysis the corrosion potential of an electrode generally, with increasing dose, becomes more positive (i.e. moves to the hydrogen peroxide redox equilibria). Thus, radiolysis of water tends to result in an oxidising environment which, for passive alloys, will result in a significant risk of localised corrosion, especially stress corrosion cracking.

Where the gaseous products of reaction are allowed to equilibrate with the external environment then the reaction equilibria may be shifted to become net reducing (i.e. with hydrogen overpressure). This effect may be used to reduce the corrosion potential towards the equilibrium hydrogen electrode at which value most alloys are close to or within the immunity regime for corrosion. Thus, in BWR and PWR systems, hydrogen overpressures in the range 20-25 cm^3 H$_2$/kg are commonly used to suppress oxidative radiolysis products and to ensure that the corrosion potential of stainless steel in the reactor cores is close to -230 mV (v. the Standard Hydrogen Electrode) commonly given as a safe limit. Additionally, especially in BWRs, the addition of small quantities of noble metals into the core coolant catalyses the hydrogen/oxygen recombination reaction that otherwise can be somewhat sluggish.

1.3 Forms of aqueous corrosion

1.3.1 General corrosion

General corrosion is characterised by damage that results in a more-or-less uniform thickness loss from a metal where generally the whole surface becomes increasingly roughened with

time. It is important to note that in situations the anodes and cathodes can become localised, for example due to differences in local concentration of cathodic reactant or due to the geometry of the component, then relatively rapid local corrosion will occur in those areas that are anodes. This can most clearly be appreciated, for example, where a section of steel is piled into the ground. Those areas of the steel close to the surface will be located in a region of higher oxygen concentration and will become cathodes. Conversely, those areas at greater depth will be located in regions of lower oxygen concentration and, hence, will become anodes.
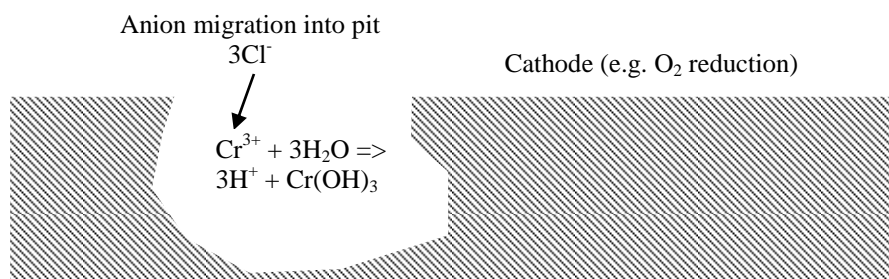
1.3.2 Pitting and crevice corrosion

Localised corrosion is characterised by damage that occurs preferentially at discrete sites on a material surface and may result in the formation of pits, cracks, grooves, etc. A large cathode-to-anode area ratio is generally required in order to form an intense local anode. Since this is most easily obtained in metals that are passive then localised corrosion most commonly occurs on materials that are passive.

Pitting is a form of localised corrosion damage that results in the formation of small defects or pits, often associated with a cover of corrosion product or perforated metal over the pit. True pitting only occurs on metal surfaces that are passivated by a protective film and it is the breakdown of this passive film that results in the localisation of the anode region. Breakdown of the passive film is a time-dependent process that is also a function of many other variables, including: electrochemical potential, composition of the alloy, composition of the environment, mass transport in the environment, etc. Most pitting events are stochastic and merely transient, lasting for a short time only before re-passivation. However, as the electrochemical potential becomes more positive and as the environment becomes more corrosive active pits survive for increasingly longer times. Eventually, a pit grows sufficiently large such that it the local solution chemistry in the pit becomes significantly different from the bulk solution chemistry and hence stable and severe localised corrosion damage then becomes a possibility.

Active (as opposed to metastable) localised corrosion is generally dependent upon the development of a stable local solution chemistry that is different from the bulk solution. All active pits are, by definition, anodes and the external (passive) surface is the cathode. Since the area of the cathode is very large compared to the anode, the cathodic current per unit area (or cathodic current density) is small while the anodic current density is large; since the current density defines the corrosion rate, this accounts for the relatively rapid corrosion rate in active pits. Once established, active pits tend to be stabilised. This is because for every metal ion (cation) that is produced a corresponding anion is required to migrate into the pit solution to maintain electroneutrality. Additionally, if halides are present (chloride is particularly ubiquitous) the metal ions are subject to the hydrolysis reaction, e.g. for chromium:

$$Cr^{3+} + 3H_2O \rightleftharpoons Cr(OH)_3 + 3H^+ \text{ (acidification)} \qquad \textbf{... (22)}$$
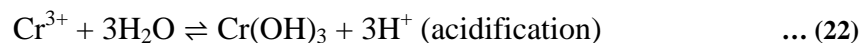
Hence, the pit solution tends to become more concentrated and more acidic both effects conspiring to increase the local pit anodic dissolution rate, Figure 9.

Anion migration into pit
$3Cl^-$

Cathode (e.g. O_2 reduction)

$Cr^{3+} + 3H_2O =>$
$3H^+ + Cr(OH)_3$
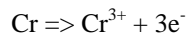
$$Cr => Cr^{3+} + 3e^-$$ Metal substrate

Figure 9: Schematic diagram illustrating the chemistry in a pit

Crevice corrosion has a similar mechanistic basis to pitting corrosion however the local solution heterogeneity that initiates the corrosion process is intrinsic to the physical geometry of the component or system. Thus, a sufficiently tight crevice between two materials constitutes a diffusion barrier to the mass transport of species in and out of the crevice. This becomes significant when a species that takes part in the corrosion process diffuses slowly in the crevice. For example when oxygen, initially present throughout the system, gets consumed within the crevice an anode will preferentially form within the crevice with the cathode located outside the crevice. Alternatively or additionally, corrosion will increase the local metal ion concentration since the crevice restriction will limit the amount of exchange to the external environment. Also, as in a pit, metal ion hydrolysis will tend to lower the crevice pH thus increasing the local anodic dissolution rate in a similar manner to pitting.

1.4 Corrosion control

The four main methods for controlling the corrosion of a material or component are: (a) materials selection, (b) environmental modification, (c) electrochemical control and (d) application of a protective coating. These methods may be used either individually or in combination and generally, the choice is often based on the most cost-effective option able to achieve the required performance and lifetime characteristics.

Successful materials selection is based upon identifying and delivering the key materials property/ performance requirements of the product that is being designed in relation to:

- Functionality – appropriate combinations of physical, thermal, mechanical, electrical and/ or magnetic properties in combination with appropriate formability and ease of fabrication.
- Appearance – appropriate formability and ease of fabrication with surfaces amenable to appropriate finishing that might include processes such as colouring, patterning and texturing.
- Durability – predictable resistance to fracture, wear, corrosion, or other deterioration processes throughout the design life of the product.
- Economy – acceptable cost and availability.

Practically, cost-effective corrosion control often requires the use of a relatively cheap material that serves the required mechanical or physical function (e.g. a carbon or low-alloy steel). In such cases *in situ* environmental modification is required to control the corrosivity of the environment. There are a variety of technologies to available achieve this end, and selection depends upon the specific details of the particular application, generally driven by the requirement to achieve acceptable performance for minimum cost. The scientific basis behind environmental modification can be divided into two fundamentally different underlying methods:

- Corrosive agent removal: This involves deliberate modification of an environment in order to reduce its chemical and/or electrochemical activity towards a substrate material by removal of specific corrosive reagents.

- Protective barrier inducement: This involves the deliberate addition of a chemical species that interacts in some way with the corroding substrate so as to form a protective barrier that reduces the corrosion rate to an acceptable level.

It is important to note that these strategies may be combined together (and indeed also combined with one of the *ex situ* corrosion control methods – for example the addition of corrosion inhibitors into paints) in order to achieve the desired performance.

Electrochemical corrosion control generally involves the application of a cathodic potential to a material so that the net anodic reaction rate is reduced (and, consequently the net cathodic reaction rate is increased); a method known as cathodic protection. This may be achieved either by the use of a sacrificial anode such as zinc to protect carbon steel or by application of an external potential from a DC power supply. In the latter case the potential may, in principle, be made sufficiently negative such that the material is driven into its immunity regime. However, a likely result is that the cathodic hydrogen is generated, which can result in undesirable embrittlement of materials. For materials that may be passivated in an appropriate environment, then an anodic potential may be applied in order to ensure that the passive film is successfully formed. This method, known as anodic protection, is only feasible where a passive oxide is stable over a sufficiently large range of potential but can be used in a range of environments.

1.5 Metallurgical influences on corrosion

1.5.1 Microstructure

All materials (apart from those that are amorphous or glassy in nature) have an underlying long-range structure,. This is manifested as a regular and repeating arrangement of atoms in the metal and the consequent appearance of crystallinity that is apparent over various lengths from the nano (< 100 nm), through the micro (0.1 to ~10 µm) the mesa (10 µm to ~1 cm) to the macro (> 1 cm). Generally the materials microstructure influences, at a fundamental level, the materials performance, both mechanically and in terms of corrosion resistance.

A detailed discussion of metallurgy is beyond the scope of this chapter however, certain principles are worth describing. All alloys of interest in the nuclear context are crystalline and, consequently have a structure that is dependent on how they have been manufactured and subsequently processed. For example, a typical microstructure for equilibrium (thermally) annealed austenitic stainless steel is shown in Figure 10, where the individual crystal grains (of approximate dimension ~ 50 µm) can be easily seen. Second phase particles are also present in alloys and arise either from deliberate alloying addition (e.g. the presence of carbides in steel) or from adventitious contamination or otherwise unwanted constituents. In the latter case these unwanted precipitates may influence corrosion processes in a fundamental manner (e.g. surface breaking MnS precipitates in stainless steel are the primary location for the initiation of pitting corrosion).
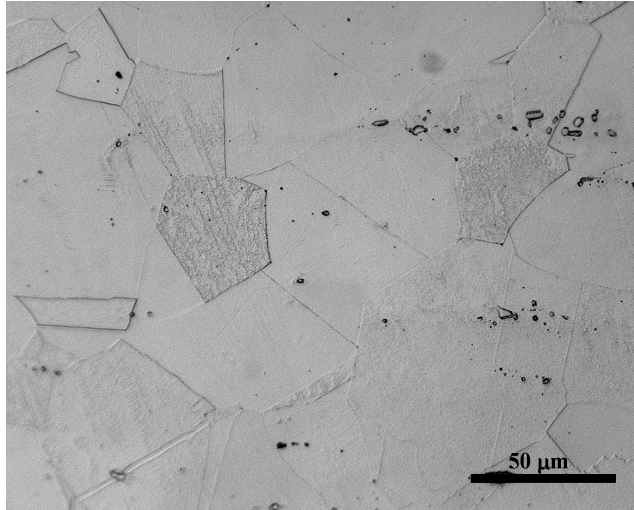
Figure 10: Microstructure of annealed austenitic stainless steel; the large equiaxed grains are austenite while a small amount of retained delta-ferrite can be seen, particularly at the top left.

Each individual grain comprises a unique crystal within the microstructure where the atoms are regularly ordered in a repeating fashion. However, at boundaries between these grains, the atomic structure is locally disordered. Grain boundaries, therefore, provide sink sites for atomic defects such as vacancies (i.e. a local absence of an atom) and are preferential locations for atomic segregation and for the precipitation of second phase particles. In the last case, if the formation of a second phase particle at a grain boundary is associated with a change in local alloy composition close to the grain boundary, then intergranular corrosion damage can take place, Figure 11.
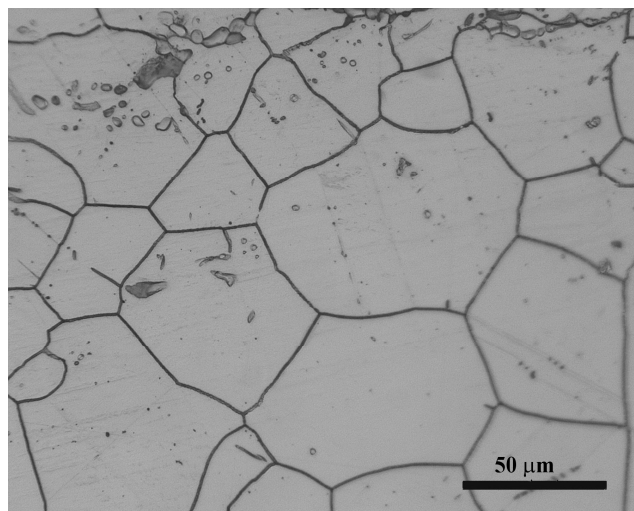
Figure 11: Intergranular attack of sensitised austenitic stainless steel; the sample shown in Figure 10 has been heat treated at 650°C for 24 hours in order to precipitate chromium carbide at the grain boundaries. This has depleted the local chromium content so that when the sample is etched, severe ditching occurs along the grain boundaries.

1.5.2 Processing

During fabrication, materials are commonly shaped either by a metal working process (e.g. rolling, bending etc.) or by metal removal (e.g. cutting, machining, etc.). The permanent deformation of a material after an applied load is removed is known as "plastic deformation"

(e.g. like wet clay). This can be contrasted with "elastic deformation" where the deformation is recovered after removal of the applied stress (e.g. like rubber). Plastic deformation in an metallic alloy involves the motion of atomic defects called dislocations which move in preferred atomic directions and orientations under the application of a shear stress or load. Importantly, plastic deformation causes grains in the alloy microstructure to individually deform and partially rotate to align with these preferred directions. Deformation, for example as a result of cold work, gives rise to a number of factors that can influence the corrosion process including:

- An increase in the overall stored energy within the alloy (due to the accommodation of strain) and, hence, residual local stresses (tensile and compressive); residual tensile stresses have an adverse influence on the risk of stress corrosion cracking.

- The formation of localised features known as slip bands within each alloy grain. These are regions of greater atomic disorder in the microstructure, provide preferential pathways for diffusion and are also implicated in stress-corrosion cracking in high temperature water environments.

Fabrication of components may also involve initial, intermediate or final heat treatment, metal joining (i.e. welding) and cladding (i.e. metal deposition). Heat treatments are used to control material properties (e.g. annealing/removal of stored strain energy from cold work and control of microstructural features such as second phase particles/precipitates). It is important to appreciate that correct heat treatment or welding should be performed and the incorrect processes, especially heat treatments, can increase the risk factors for corrosion and stress-corrosion.

1.5.3 Radiation damage

Radiation emitted in a reactor core and by radioactive isotopes consists either of sub-atomic particles (i.e. helium nuclei (α), high-energy electrons (β) and neutrons (n)) or short wavelength electromagnetic energy (γ). Ionising radiation specifically may be defined as radiation that imparts significant energy to the matter with which it interacts. Thus, radiation may affect the physical properties of the material, and it corrosion rate, by a number of processes that are described briefly below. The corrosion rate of passive metals is dependent upon the number and type of free charge carriers (either ionic or electronic) in the protective surface film. Ionising radiation of all types can alter the type and density of charge carriers and, hence, alter the electronic and ionic conductivity of protective films, which will adversely influence the corrosion rate.

The interaction of charged particles (i.e. α and β) with the metal will alter the corrosion potential. Thus, the capture of helium ions or electrons will, respectively, tend to increase the rates of the anodic or the cathodic processes. In both cases the overall corrosion rate would be expected to increase. Radiation that is specifically in the form of energetic particles (e.g. neutrons and protons) will interact with atoms in the metallic lattice in a number of ways generally via elastic and inelastic collisions.

- Atoms may be displaced from their initial atomic position by collision with a particle, thus producing a vacancy-interstitial pair.

- Atoms may interact with the incoming particle, for example by capturing a neutron. This may result in transmutation of the atom.

- Incoming particles may loose all their energy and be captured within the atomic lattice.

The first of these processes results in an increase in the lattice vacancy concentration and a consequent increase in diffusion rate. Differential rates of vacancy generation around grain boundaries can give rise to radiation-induced segregation for example where chromium locally depletes this increasing the risk of intergranular corrosion. The general disruption to the lattice structure as a consequence of radiation damage also results in many other significant changes to material properties. For example, both radiation-induced softening (e.g. due to local dissolution of second phase particles) or hardening (due to the atomic displacements causing an increased in stored energy) can occur.

1.6 Mechanical influences on corrosion

1.6.1 Fracture

Conventionally, a material under a static load below its yield stress will not plastically deform. After yield, plastic deformation occurs whereby the material undergoes a permanent change in shape however, below its ultimate tensile stress it will not break or fracture. Macroscopic fracture under a load or stress occurs as a result of the initiation of a defect, such as a crack, which then propagates through the thickness of the material. The resistance to propagation of cracks is given by the fracture toughness of a material; glass has low fracture toughness while structural carbon steel has high fracture toughness. Note that toughness and ductility are not the same at all. For example, wet clay has a high ductility (i.e. it may be plastically deformed to large strains) but low fracture toughness (i.e. it fractures easily at a notch). The fracture toughness, K, is defined as:

$$K_I = \sqrt{\sigma.a} \qquad\qquad \text{... (23)}$$

Where: K_I is the fracture toughness in mode I loading (i.e. crack opening), σ is the stress and a is the defect (or crack) size.

Since a critical value, K_{IC}, may be defined below which no crack propagation is predicted to occur, fracture that occurs below the nominal critical value of stress intensity must, therefore, result from some other damage process that increases with time. Two main processes can cause damage accumulation (or slow crack growth); fatigue/corrosion fatigue and stress corrosion cracking. It is thus essential to determine the susceptibility of materials to these failure mechanisms as part of the development of reliable and safe structural designs.

1.6.2 Stress corrosion cracking

During service, materials are generally subject to mechanical influences that can be tensile or compressive, constant or varying. Also, residual stresses that arise from materials processing and component manufacture are likely to be present. Fortunately, high operational and/or residual tensile stresses do not normally comprise an enhanced corrosion risk for the majority of constructional alloys, including carbon steels. Unfortunately, common corrosion-resistant alloys, including austenitic stainless steels and some nickel alloys, are susceptible to stress corrosion cracking in specific combinations of material and environment, Figure 12.
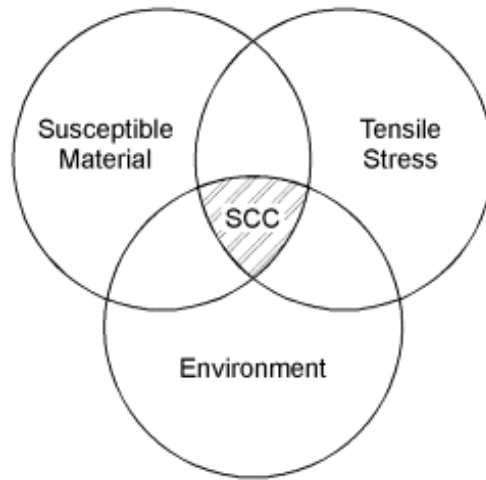
Figure 12: Schematic diagram illustrating requirements for materials' susceptibility to stress corrosion cracking (SCC)

Stress corrosion cracking almost always initiates from a small corrosion defect such from a pit or crevice as the local chemistry is similar in all cases. The defect propagates into a short-crack with dimension of the order of a grain diameter then into a long crack with macroscopic dimensions spanning from more than one grain to the full component size. The possible mechanisms of stress corrosion are varied and depend on the material + environment combination however they are all required to explain:

- Why cracks initiate and then propagate in intrinsically ductile materials?

- Why such cracks can propagate at stress intensity factors many times less than those required to cause macroscopic failure of the same material?

The propagation rate of stress corrosion cracks is generally found to be a function of the stress intensity factor, K. Thus, there is generally a threshold stress intensity value (i.e. K_{ISCC}) below which the crack propagation rate becomes very low or zero. Between this value and the stress intensity value for fast fracture (i.e. K_{IC}) the crack propagation rate, v, follows an approximate log-linear relationship with stress intensity where the rate depends on the nature of the corroding environment, Figure 13.
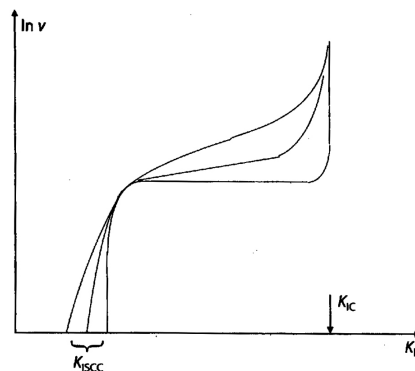

Figure 13: SCC crack growth rate as function of stress intensity factor

1.6.3 Corrosion fatigue

Cyclic stresses give rise to fatigue processes that shorten component lifetime, while corrosion tends to accelerate normal fatigue giving rise to corrosion fatigue. Fatigue is relatively well-understood and design codes exist to predict performance from the result of mechanical testing in air and in corrosive environments (respectively for fatigue and corrosion fatigue). Two main types of experimental test are commonly performed: measurement of the applied stress v. number of cycles before failure (S-N curves) and measurement of the crack growth rate as a function of the applied stress intensity factor (Paris Law curves). The latter type of measurement is more complex to carry out but provides more design information. Typically, the logarithm of the crack growth rate is found to be linearly dependent on the stress intensity over a range of values:

$$\log\left(\frac{da}{dN}\right) = m\log(\Delta K) + \log C \qquad \textbf{... (24)}$$

Where: a is the crack length and N is the number of cycles (hence da/dN is the crack growth rate at the Nth cycle), m is the slope of the line, ΔK is the range of stress intensity, and C is a constant. Using this approach it is possible to make a quantitative prediction of residual life for defects and also to quantify the effects of corrosion on fatigue life. For example, for fatigue in air a threshold stress or stress intensity can be found below which crack propagation is low or zero. The effect of corrosion typically is to lower (or remove) the threshold and to increase the crack growth rate.

1.7 Glossary of corrosion terms

Active: freely corroding; neither passive nor immune.

Activity (thermodynamic): the thermodynamic activity of an entity, i, is $a_i = \exp(\Delta G /RT)$ where ΔG is the free energy increase of 1 mol of i when it is converted from a standard state (defined as when $a_i = 1$) to any other activity $a_i = x$.

Anion: a negatively charged ion; it migrates to the anode of a galvanic cell.

Anode: the electrode in a galvanic at which electrochemical oxidation takes place.

Anaerobic: air or uncombined oxygen being absent.

Austenite: the γ-modification of iron, having a face centred cubic lattice.

Bimetallic (galvanic) corrosion: corrosion of two metals in electrical contact, in which one metal stimulates attack on the other and may itself corrode more slowly than when it is not in such contact; galvanic is often used in place of bimetallic.

Cathode: the electrode of a galvanic or voltaic cell at which electrochemical reduction takes place.

Cathodic reactant: species which is reduced at a cathode.

Cation: a positively charged ion; it migrates to the cathode in a galvanic or voltaic cell.

Concentration Cell: a galvanic cell in which the e.m.f. is due to differences in the concentration of one or more electrochemically reactive constituents of the electrolyte solution.

Corrosion (of metals): the process of wastage of metals brought about by electrochemical and/or chemical interaction with their environment.

Corrosion control: control of the corrosion rate and form of attack of a metal of a given metal/environment system at an acceptable level and at an economic cost.

Corrosion fatigue: failure by cracking caused by reversing alternating stress in the presence of a corrosive environment.

Corrosion product: metal reaction product resulting from a corrosion reaction; although the term is normally applied to solid compounds it is equally applicable to gases and ions resulting from a corrosion reaction.

Corrosion rate: the rate at which a corrosion reaction proceeds. It may be expressed as a rate of penetration mm y^{-1}, mm s^{-1} etc. (inches per year or ipy is still sometimes used), or as a rate of weight loss per unit area, for example: g m^{-2} d^{-1}, mg dm^{-2} d^{-1} (mdd) etc. It may also be expressed as the equivalent current density.

Crevice corrosion: localised corrosion resulting from the presence of a crevice in a fabricated component or between two surfaces, at least one of which is a metal.

Critical humidity: the relative humidity at and above which the atmospheric corrosion rate of a metal increases markedly.

Critical pitting potential: the most negative potential required to initiate pits in the surface of a metal held within the passive region of potentials (it varies with the nature of solution, temperature, time, etc.).

Current (I): the rate of transfer of electric charge; unit current is the ampere (A) which is the transfer of 1 coulomb/second (1 C/s).

Current density (i): the current per unit area (usually geometric) of surface of an electrode (units: A m^{-2}, A cm^{-2}, mA m^{-2} etc.)

Deposit attack: localised corrosion (a form of crevice corrosion) under and resulting from a deposit on a metal surface.

Differential aeration: Differences in oxygen concentration in the electrolyte solution in contact with a metal. Differential aeration stimulates corrosion of that area where the oxygen concentration is lower, which becomes the anodic site.

Diffusion: Movement of atoms, ions or molecules under an activity (or concentration) gradient.

Diffusion layer: the thin layer of solution adjacent to an electrode through which transport of species to or from the electrode surface occurs by diffusion rather than by convention.

Electrode: an electron conductor by means of which electrons are provided for, or removed from, an electrode reaction.

Electrode Potential (E): the difference in electrical potential between an electrode and the electrolyte with which it is in contact.

Electrolyte: a substance, liquid or solid, which conducts electrical current by movement of ions (not of electrons).

Electro-migration: movement of ions under an electric field.

Erosion: loss of material mechanically by impact of a liquid, gaseous or particulate environment.

Erosion-corrosion: the wastage of a material caused by the conjoint action of erosion and corrosion by a liquid or gaseous environment, with or without solid particles.
Faraday's constant (F): the quantity of electric charge involved in the passage of one Avagadro number (or one mole) of electrons. The value of F (universal) is 96 485 C mol^{-1}.

Fatigue: failure of metal under conditions of repeated alternating stress.

Ferrite: the body-centred cubic form of iron (α-iron) and the solid solutions of one or more elements in body-centred cubic iron.

Film: a thin coating of one material on another, not necessarily thick enough to be visible.

Galvanic cell: an electrochemical cell having two electronic conductors (commonly dissimilar metals) as electrodes.

Galvanic corrosion: corrosion associated with a galvanic cell

Galvanic series: a list of metals and alloys based on their relative potentials in a given specified environment.

Hydrogen electrode: an electrode at which the equilibrium H^+ (aq.) $+ e \leftrightarrows H_2$, is established. By definition, at unit activity of hydrogen ions and unit fugacity of hydrogen gas the potential of the standard hydrogen electrode $Eq_{H_+}/H_2 = 0.00$ V.

Immunity: the state of a metal whose corrosion rate is low or negligible by virtue of its sufficiently negative electrochemical potential.

Inhibitor: a substance added to an environment in small concentrations to reduce the corrosion rate.

Intergranular corrosion: preferential corrosion at grain boundaries.

Internal oxidation: formation of particles of corrosion product (usually oxide) within the metal matrix beneath the metal surface.

Ion: an electrically charged atom or molecule.

Localised corrosion: accelerated corrosion at certain sites only of a metal surface due to spatial separation of anodes and cathodes; examples include pitting corrosion, stress-corrosion cracking and intergranular corrosion.

Open-circuit potential: the potential of an electrode (relative to a reference electrode) from which no net current flows, so that the anodic and cathodic reactions occur at an equal rate.

Oxidation: loss of electrons by a species during a chemical or electrochemical reaction; addition of oxygen or removal of hydrogen from a substance.

Passivation Potential: the potential at which a metal in the active state becomes passive.

Passivity: the state of a metal in which a low corrosion rate is brought about by reaction with its environment under a high anodic driving force through formation of a surface barrier film, usually an oxide.

pH: a measure of the hydrogen ion activity defined by pH = -log aH^+ where aH^+ is the activity of the hydrogen ion.

Pitting (corrosion): the formation of small holes in an otherwise passive metal surface as a consequence of locally accelerated corrosion.

Pitting potential: minimum potential (least noble or least positive) at which a metal undergoes permanent pitting corrosion.

Polarisation Curve: A plot of the current density flowing from an electrode against the electrode potential, often presented on a logarithmic current density axis.

Potential-pH Equilibrium Diagram (Pourbaix Diagram): diagram of the equilibrium potentials of electrochemical reactions as a function of the pH of the solution.

Reduction: a chemical or electrochemical reaction in which a species gains electrons; the removal of oxygen or the addition of hydrogen.

Reference Electrode: an equilibrium (reversible) electrochemical half-cell of reproducible potential against which an unknown electrode potential can be measured; examples of those commonly used in corrosion are the Pt, H_2/H^+ (the hydrogen electrode), $Hg/Hg_2Cl_2/Cl^-$ (the calomel electrode).

Relative humidity: the ratio of the amount of water vapour present in the atmosphere at a given temperature to the amount required for saturation at the same temperature, expressed as a percentage.

Sensitisation: susceptibility to intergranular attack in a corrosive environment resulting from heating a stainless steel at a temperature and time that results in precipitation of chromium carbides at grain boundaries.

Standard electrode potential: the equilibrium potential of an electrode reaction when the components are all in their standard states.

Stress intensity factor: a fracture toughness parameter used for assessing susceptibility to fast fracture, stress corrosion cracking, etc.

Stress-corrosion cracking: damage produced by the combined action of corrosion and static tensile stress (internal or applied).

Uniform corrosion (general corrosion): corrosion in which no distinguishable area of the metal surface is solely anodic or cathodic, i.e. anodes and cathodes are inseparable, cf. localised corrosion.

Weld decay: localised attack of austenitic stainless steels at zones near a weld, which results from precipitation of chromium carbides.

1.8 Further reading

"Shreir's Corrosion", eds. Tony Richardson, Bob Cottis, Rob Lindsay, Stuart Lyon, David Scantlebury, Howard Stott and Mike Graham, Elsevier (2010)

"Handbook of Corrosion Engineering", Pierre R. Roberge, McGraw-Hill (2000)

"Electrochemical Techniques in Corrosion Science and Engineering", R.G. Kelly, John R. Scully, David W. Shoesmith, Rudolph Buchheit, Marcel Dekker (2003)

1.9 References

1. "Corrosion of metals and alloys - basic terms and definitions", ISO 8044-1986

2. "Current cost estimates and national strategies to minimize the impact of corrosion", pub. NACE International, Houston, USA (1999)

3. "Prediction of the effects of radiation for reactor pressure vessel and in-vessel materials for 60 years plant life"; PERFORM 60: European Union FP7 Collaborative Research Project

4. J. Keir, Phil. Trans. Royal Society, Vol.80, 359-384 (1790)

5. C.F. Schonbein and M. Faraday, Phil. Mag. 9, 53,57, 122 (1836)

6. Froment, M., Keddam, M., Morel, P., Compt. Rend. 253, 2529 (1961)

7. Calculated using HSC Thermochemical Modelling Software, Outotec, Finland

8. V.C. Levich, "Physicochemical Hydrodynamics", Prentice-Hall, NJ, USA (1962)