Metallurgy And Metallic Materials Summary

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Abstract

This is a summary for Metallurgy and Metallic Materials course that was conducted by Mohamed Ossama, a materials and corrosion engineer. The course aims to give a scientific background with regards to material selection process, and its contributing factors.

1 Introduction

The engineering of materials is science that concerns with extracting, processing, manufacturing, and applying materials in industry and other engineering fields.

2 Engineering Of Materials Classifications

First category is based on the existence or absence of metals.

2.1 Metallic

Non-organic materials, and usually a combination of metallic elements (e.g. Fe, Ti, Al, Ag).

2.1.1 Ferrous

Materials that are mainly made of iron metal.

- Carbon Steel: common type of carbon-iron alloy with $1.0\% \succ C \succ 0.3\%$.
- Cast Iron: carbon-iron alloy with 2% of C.
- Stainless Steel: corrosion-resistance alloy with $\succeq 11\%$ of Cr.

2.1.2 Non-Ferrous

Materials that are mainly made of non-iron metals.

- Cu-alloy: corrosion-resistance alloy primary made of copper (e.g. brass $\iff$ Cu + Zn).
- Ni-alloy: corrosion-resistance alloy primary made of nickel (e.g. UNS 2200 (Nickel 200)).
- Ti-alloy: corrosion-resistance alloy primary made of titanium.

2.2 Non-metallic

2.2.1 Polymers

Class of natural/synthetic substance compound made of very large molecules. *Outside the scope of this course.*

2.2.2 Ceramics

Non-metallic, non-organic, and non-reactive materials with hard, brittle, heat-resistance, and corrosion-resistance properties. *Outside the scope of this course.*

3 Material Properties

Material properties are dependent on three factors :

1. Mechanical work
2. Heat treatment
3. Chemical composition

we manipulate these factors in order to achieve the desired material properties.

3.1 Yield Strength

Material resistance to yield (After the yield, permanent plastic deformation occurs).

3.2 Ultimate Strength

The maximum stress that a material can endure before failure.

3.3 Fracture

Material Failure.

3.4 Hardness

Material resistance to notch formation, however, more hard materials are more susceptible to cracking during processing, forming, or welding.

3.4.1 Hardness Test Methods

- Brinell Method (HB)
- Rockwell Methods (HRC, HRB)
- Vickers Method (HV)

3.5 Toughness

Toughness is defined as a materials capacity to absorb energy, which is dependent upon strength as well as ductility.

3.5.1 Toughness Test Methods

- Charpy V notch: Most applicable method.
- Drop weight nil-ductility: Used for brittle materials.
- Crack tip opening displacement: Used for measuring flaw size.

3.5.2 Factors Affecting Material Toughness

- Chemical composition
- Materials processing
- Heat treatment

3.5.3 Ductile To Brittle Transition

This characteristics is accompanying solid state phase transformation changing fracture characteristics from ductile to brittle whenever metal temperature is decreased to lower levels (29^oC for carbon steel materials).

3.6 Wear Resistance

Wear of metal is defined as plastic displacement of surface or near surface material by contact with other metals, non metallic solids, flowing liquids, solid particles contained in flowing liquids.

3.6.1 Metallic Against Non Metallic Abrasive (Erosion)

- Erosion of impellers by sands contained in flowing liquid.
- Erosion of earth removing devices by abrasives in dry sand.

3.6.2 Metal Against Metal

Sliding and/or Rolling: for example, wear of shaft in bearing.

3.6.3 Liquid Or Vapor Impingement On Metal

Cavitation (Cavitating Venturis) , turbulent, and high velocity flowing liquids.

3.7 Creep Stress Relieving

Creep is defined as a very slow plastic strain increased by time and temperature (time and temperature dependent) for stressed materials.

3.8 Rupture

Rupture is material failure due to creep.

4 Materials Categories And Selection

4.1 Degradable Materials

4.1.1 Carbon Steel

Carbon steel is a steel with $0.05\% \preceq C \preceq 2.1\%$ by weight.

Properties:

1. The most common material used today.
2. Known of is excellent mechanical properties high availability.
3. Economically suitable.
4. Has poor corrosion resistance properties.
5. Usually requires corrosion control techniques.

Types:

1. Low carbon steel: $\preceq 0.3$ carbon.
2. Medium carbon steel: $0.3\% \prec C \preceq 0.6\%$.
3. High carbon steel: $0.6\% \prec C \preceq 1.0\%$.

4.2 Corrosion Resistant Alloys CRA

Modified metals by adding alloys that prompt greater corrosion resistance.
Used as:

1. Solid
2. Clad
   (a) 316L
   (b) 825
   (c) 904L
   (d) C-276, 625 for severe service
3. Weld Overlay

4.2.1 Stainless Steels

Stainless Steel is defined as a ferrous alloy containing a minimum of 11 % of Cr.
Properties:

- Known of its superior resistance against corrosion.
- Known of its good mechanical properties.
- Divided into five families according to their crystallographic structure.

Stainless Steel families are:

- Austenitic Stainless Steel.
- Ferritic Stainless Steel.
- Martensitic Stainless Steel.
- Super Stainless Steel.
- Duplex Stainless Steel.

4.2.2 Austenitic Stainless Steel

- A type of an austenite FCC (face centered cube structure).
- Non-magnetic.
- None hardenable by Heat treatment.
- Hardenable by cold working.
- Have high corrosion resistance properties.

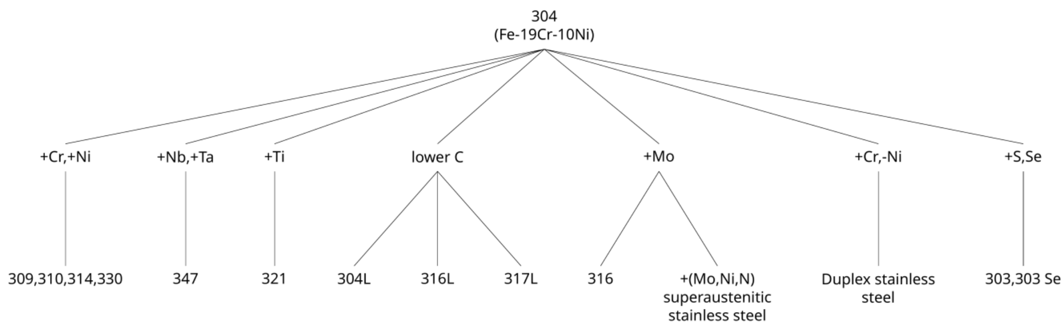

Figure 1: Stainless Steel families

- High temperature strength.
- Good weldability.
- Contains a min. of 18% Cr and 8% Ni as the main alloying elements
- Recognized by the AISI (American Iron and Steel Institute) as the 3xx series, e.g. 304 , 316.

4.2.3 Super Austenitic Stainless Steel

- The most famous super stainless steel is the 6-moly SS with PREN $>$ 40.
- Super stainless steel have been developed to cover some weakness in corrosion resistance.
- Mainly developed to combat chloride stress corrosion cracking that occurs to all austenitic grades.
- The other famous SS type is the AISI 904 which is considered to be a non ferrous alloy due to its high Ni content.

4.2.4 Ferritic Stainless Steel

Ferritic Stainless Steel included within the AISI 400 series

- Cr is 11-30 %.
- Ferro magnetic.
- Not hardened by heat treatment.
- Used for nitric acid services, water, food processing, automobile trims and architectural applications.

- Their impact resistance is poor.
- Their weldability is poor.
- The general purpose grade of this stainless steel family is grade 430 which contains 17 Cr.
- Contains Cr and Mo as the major alloying elements.

4.2.5 Martensitic Stainless Steel

- Martensitic SS are hardenable grades.
- Resist high temperatures, used in turbine blades.
- Have a fair corrosion resistance and are only used in mild environments.
- The most common grade is grade 410.
- These grades are difficult to weld.
- Their low temperature impact resistance is also poor.
- Contains mainly Cr as the major alloying element.
- The cheapest stainless steel.

4.2.6 Duplex And Super Duplex Alloys

- Approximately The ferrite content shall be within the range 40 to 60 %.
- Ferrite forming alloys such as Mo and Cr are present as well as Ni as austenitic stabilizer.
- Duplex contains Mo for more resistance Chloride pitting .
- Welding of duplex should be controlled and monitored closely where the austenite phase could turn to ferrite.
- Super duplex SDSS has CR % $\succeq$ 25 ; PREN (Pitting resistance equivalent number) $\succeq$40.

4.2.7 Nickel-alloys

- Ni is a noble metal, this is why it is known of it superior resistance to corrosion.
- Ni forms a protection layer of nickel oxide.
- Ni and Ni alloys are being used extensively in industry.
- Its relatively high cost relative to the carbon steel or to the conventional stainless steel grades , resembles the only problem.

Ni and its alloys are found as :

- Ni (Alloys 200 and 201)
  1. Corrosion rates in waters contaminated or aerated is less than 0.1 $^{mm}/_{year}$.
  2. Not resistant to stagnant seawater.
  3. Resistant to all salt solutions at all concentrations.
  4. Resistant to of oxidizing and reducing acids.
- Nickel Molybdenum alloys (Alloy B-2).
  - Molybdenum is a silvery, shiny metal that belongs to the Group 6A, second transition series of the Periodic Table. It has the 6th highest melting point and is the 54th most abundant element in the world. The addition of molybdenum ensures good resistance to chloride pitting and to reducing acids in general. Also alloy B2 is known of its immunity against stress corrosion cracking.
- Ni Cu alloys (Alloys 400 ,K 500 , Cupronickel alloys 90,10,70, and 30.
  1. (Alloy 400 Monel) Si 65 % Ni, 30 % Cu, is resistant to HCl , to alkaline and neutral salts.
  2. Most famous application of Monel , it is used in the overhead section in crude distillation units.
     (a) Monel:a group of nickel alloys, primarily composed of nickel (from 52 to 67%) and copper, with small amounts of iron, manganese, carbon, and silicon.
  3. Cupro nickel alloys 90/10 & 70/30 were mainly developed to be used as piping for the marine atmospheres.
- Nickel Chromium Iron alloys (Alloys 600 & 800).
  - Due to the high Chromium content, these two alloys were developed to be used in corrosive gases at extremely high temperatures under oxidizing conditions.
- Nickel Chromium Molybdenum alloys (C-276 , C-4 & alloy 625).
  - Cupronickel or copper-nickel (CuNi) is an alloy of copper that contains nickel and strengthening elements, such as iron and manganese.Nickel Chromium Molybdenum alloys combine the good resistance properties of the last two families they considered like the super nickel alloys where they are resistant to nearly every single environment and hence their cost is considerably higher than the other Ni alloys.

4.2.8 Copper-alloys

4.2.9 Titanium-alloys

- Ti is widely used in aerospace, medical, and petroleum industries.
- known of its excellent corrosion resistance properties.
- Used in seawater cooling, seawater valves and fittings, data logging systems, cathodic protection anodes, pumps and valves as well as underwater operations.

4.3 Material Selection

1. Process flow diagrams (PFD) showing design/operating/ upset conditions of:
   (a) Temperature (min. & max.)
   (b) Pressure
2. Stream chemical analyses showing the corrosive constituents and their concentrations:
   (a) H_2O
   (b) Dissolved gases H_2S, O_2,CO_2
   (c) Cl^-
   (d) TDS (total dissolved salts)
   (e) Pressure
   (f) TAN (total acid number) for crude oil
   (g) Total Sulfur Content

Materials selection is made either using a degradable material (carbon steel) with the addition of a corrosion allowance " with or without the addition of a corrosion control technique (e.g. coating, cathodic protection, etc.) , or using a corrosion resistant alloy (a material that doesn't readily corrode in the environment), such as the use of stainless steel or nickel alloys. The decision either to go for a CS or for CRA depends mainly on economics as well as other factors such as replacement capabilities, maintainability, criticality of service, etc.The selection process recommended ranking is (1-most favorable economically) :

1. carbon steel
2. stainless steel
3. duplex
4. super duplex
5. Ni-alloys

5 Crystallographic Structures And Grain

A crystalline material is the arrangement of atoms in a repeating or periodic array over large atomic distances.In that regard, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms.

5.1 BCC

Body-centered cubic (BCC) is a common metallic crystal structure has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. The following equation is used to find the unit cell length a in relation to radius R:

$$a = \frac{4R}{\sqrt{3}} \tag{1}$$

5.2 FCC

Face-centered cubic (FCC) is where atoms arranged in each cube corner along with an atom at the center of each face. The following equation is used to find the unit cell length a in relation to radius R:

$$a = 2R\sqrt{2} \tag{2}$$

5.3 Grain

Small or even microscopic crystals which form, for example, during the cooling of many materials (crystallization). A very important feature of a metal is the average size of the grain. The size of the grain determines the properties of the metal.

5.4 Grain Boundaries

The grain boundary refers to the outside area of a grain that separates it from the other grains. The grain boundaries separate variously-oriented crystal regions (polycrystalline) in which the crystal structures are identical. Grain boundaries are 2D defects in the crystal structure, and tend to decrease the electrical and thermal conductivity of the material.

6 Equilibrium Phase Diagram

6.1 Binary Phase Diagram Carbon-iron

we are mainly interested in the binary carbon-iron system. Eq.3 shows eutectic reaction for the iron–iron carbide system that occurs at 4.30 wt% C and 1147^{o}C.

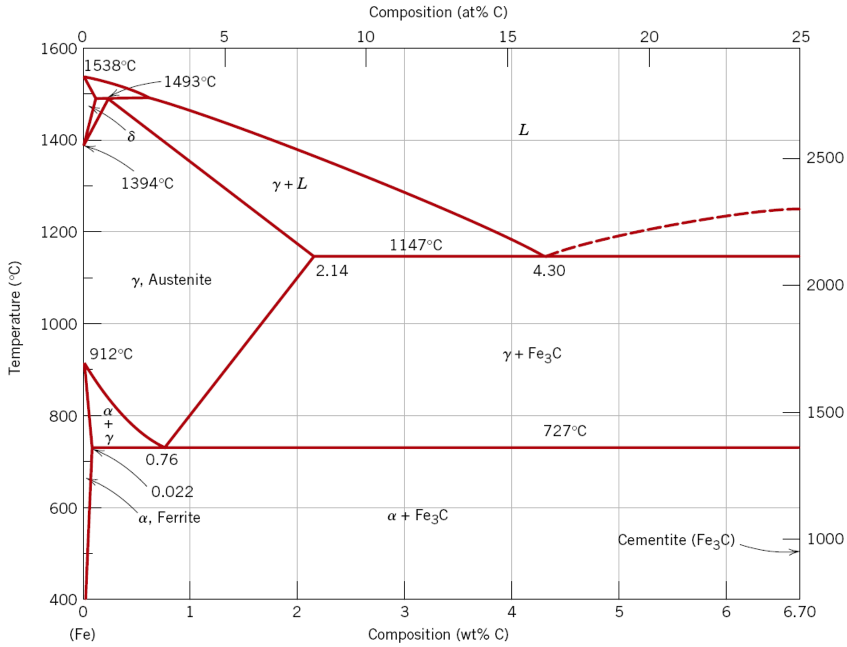

Figure 2: The iron–iron carbide phase diagram

The L meas liquid phase and Fe_3C means cementite. The liquid solidifies to make austenite and cementite phases.

$$L \rightleftharpoons \gamma \quad + \quad Fe_3C \tag{3}$$

At 0.78% carbon and 727^{o}C, a point called eutectoid invariant exists and represented by Eq.4.

$$\gamma\,(0.76\%C) \rightleftharpoons \alpha\,(0.022\%C) + Fe_3C\,(6.7\%C) \tag{4}$$

6.1.1 $\alpha - Iron$

Also called ferrite; a stable form of BCC structure between 1400-1539 ^{o}C.

6.1.2 $\delta - Iron$

Same as $\alpha - Iron$; however, with low-to-non engineering interest.

6.1.3 $\gamma - Iron$

Austenite is a solid solution of mostly iron and carbon.Austenite only forms when an iron-based alloy is heated above about 750^{o}C, but not above about 1450^{o}C.

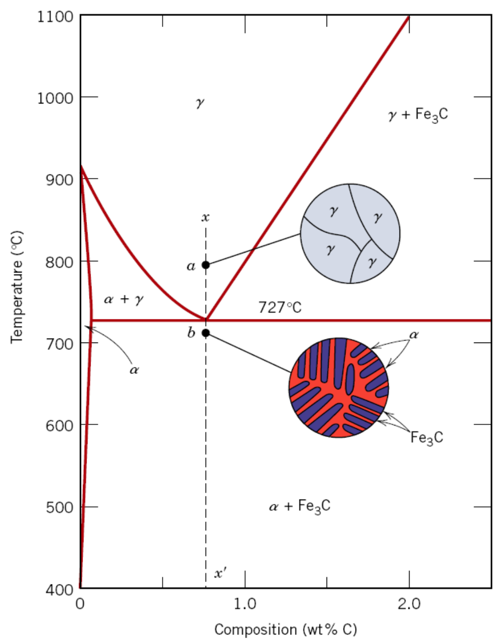

Figure 3: Schematic representations of the microstructures for an iron–carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.

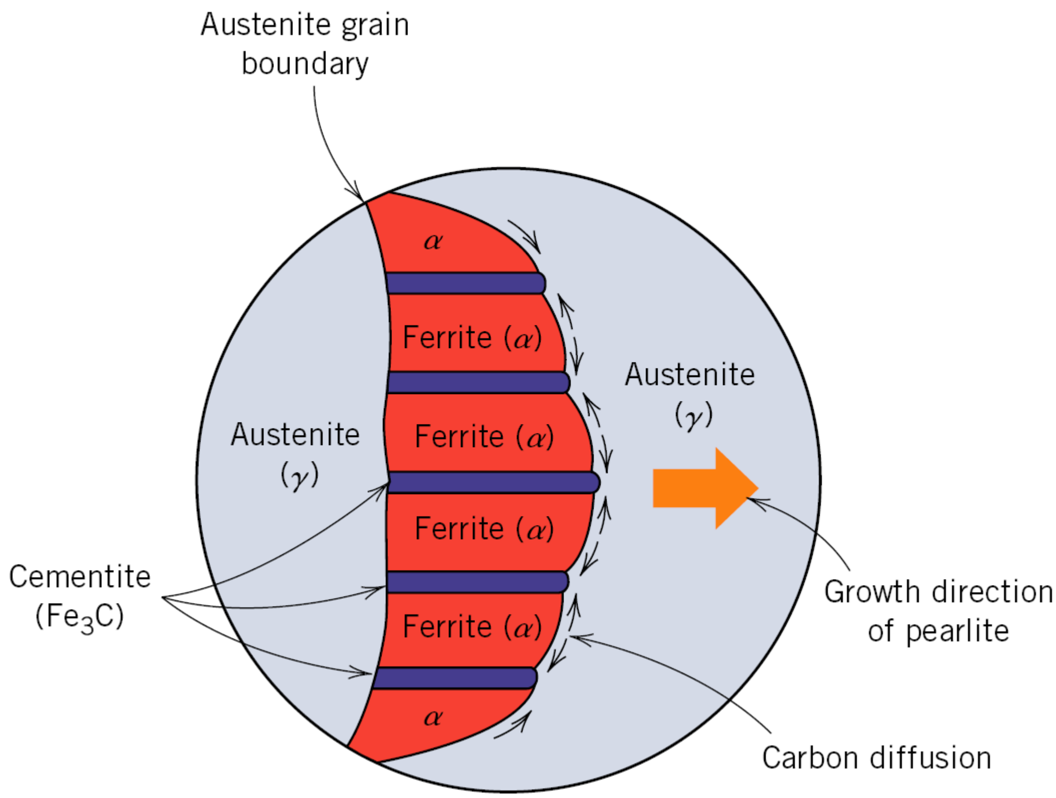

Figure 4: Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows.

6.1.4 Cementite

Also called Fe_3C, which is represented by a vertical line in the phase diagram. Thus, the carbon-iron system is divided into two categories:

1. Iron rich: with carbon content of $\preceq 6.7\%$.
2. Iron poor: made of pure graphite $\approx$100% C.

6.1.5 Pearlite

Pearlite is a mixture of ferrite and cementite forming distinct layers or bands in slowly cooled carbon steels.

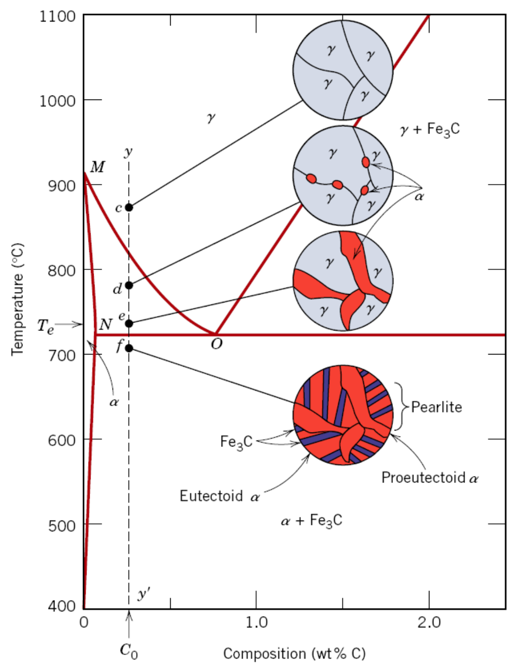

Figure 5: Schematic representations of the microstructures for an iron–carbon alloy of hypoeutectoid composition C0 (containing less than 0.76 wt% C) as it is cooled from within the austenite phase region to below the eutectoid temperature.

6.1.6 Martensite

Martensite is a very hard form of steel crystalline structure, and it is produced by quenching $\gamma - iron$.

6.2 Ternary Phase Diagram For Fe-Cr-Ni System

A ternary phase diagram shows possible phases and their equilibrium according to the composition of a mixture of three components (Fe-Cr-Ni) at constant temperature and pressure.

7 Heat Treatments

7.1 Normalizing

Normalizing is defined as a heat treatment process where a material is heated to a pre-decided elevated temperature, hold at that temperature for a certain period of time (usually 10-20 minutes), and then allowed to cool freely in the air to reach room temperature.

7.2 Quenching

Quenching is when material is heated up to suitable temperatures and then quenched (rapidly cooled) in oil to fully harden, varying on the kind of steel being worked on. Items that go through this are then aged, tempered or stress relieved to achieve the desired stability.

7.3 Tempering

Tempering is a heat treatment that improves the toughness of hard, brittle steels so that they will hold up during processing. Tempering requires that the metal is heated to a temperature below what's called the lower critical temperature.

7.4 Annealing

Annealing is treatment of a metal or alloy by heating to a predetermined temperature, holding for a certain time, and then cooling to room temperature to improve ductility and reduce brittleness.Annealing is also done for relief of internal stresses.

7.5 Stress Relieving

Stress relief is a process in which a material is heated to a specific temperature for a specific amount of time to reduce the internal forces acting on the material. The material is then typically cooled at a slow, controlled rate so as to avoid adding any other internal stresses to the material.

7.6 Post Heat Treatment

Holding the temperature just below transformation ($^{hour}/_{25mm}$). The process improves corrosion/cracking (stress) resistance, increase ductility, and toughness.

7.7 Process Annealing

Refining the grain size by heating to 500-650 ^{o}C for certain hours.

8 Refining And Alloying

8.1 Refining

Removing impurities such as:

- S
- P
- N_2
- O_2

8.2 Alloying

Alloying is a process in which two or more metal elements are melted together in a precise combination to form a specific material, or alloy. Refer to: (CRA-Section 4.2)

9 Time Temperature Transformation Diagram

TTT is an isothermal transformation diagrams with plots of temperature versus time (usually on a logarithmic scale).

10 Iron-carbon Materials For Casting

10.1 Ductile

Ductile iron, also known as ductile cast iron, is a durable, fatigue-resistant metal due to its spherical graphite structure.

10.2 Non-ductile

Also known as gray iron, which is a ferrous alloy which has been heated until it liquefies and is then poured into a mold to solidify.Grey cast iron is characterized by its graphitic micro-structure. Most cast irons have a chemical composition of 2.5 to 4.0% carbon, 1 to 3% silicon, and the remainder is iron.

10.3 Cast Iron Alloying

- Adding Si, and Al $\Rrightarrow$lower strength and hardness.
- Ni, Cu, Tn $\Rrightarrow$increase strength and hardness.
- Cr, Mo,W, V $\Rrightarrow$lower strength but higher hardness.

11 Corrosion Allowance

Carbon steel is the classical material that is used in construction, its performance in any atmosphere shall be determined and hence we have to determine the quantity of metal to be lost by corrosion and then account for during design.

$$CA = CR \times LT \tag{5}$$

Where:

- CA: corrosion allowance [mm]
- CR: estimated corrosion rate [$^{mm}/_{year}$]
- LT: required lifetime [year]

$$t = \left(\frac{PR}{SE + 0.6P}\right) + C.A. \tag{6}$$

$$t = \left(\frac{PR}{2\,SE + 0.2P}\right) + C.A. \tag{7}$$

$$lifetime = \frac{CA[mm]}{CR[^{mm}/_{year}]} \qquad [year] \tag{8}$$

Where:

- P: design pressure [Psi]
- R: inside radians [INCH]
- S: stress value of material [Psi]
- C.A.: corrosion allowance [INCH]
- t: minimum corroded thickness

Calculating a corrosion rate is either uniform or considering the maximum localized corrosion rate (which is always harder to quantify).

11.1 Sour Service

Exposure to Oil/ Gas environment that contain H_2S and can cause cracking of materials by the mechanisms addressed in **ISO − 15156**.

12 Standards And Specifications

1. ASME sec. II A (for Ferrous).
2. ASME sec. II B (for Non Ferrous alloys) .
3. ASTM A & B.
4. UNS (Unified Numbering).
5. AISI (American Iron & Steel).
6. Other codes such as ISO, DIN, EN.

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