UNIT-3 *CORRORSION & HEAT TREATMENT OF METALS AND ALLOYS*

Types of corrosion – effect of corrosion on mechanical properties – stress corrosion cracking –corrosion resistance materials used for space vehicles heat treatment of carbon steels – aluminiumalloys, magnesium alloys and titanium alloys – effect of alloying treatment, heat resistance alloys –tool and die steels, magnetic alloys

CORROSION

Corrosion is the deterioration of materials by chemical interaction with their environment.The term corrosion is sometimes also applied to the degradation of plastics, concrete andwood, but generally refers to metals. The most widely used metal is iron (usually as steel)and the following discussion is mainly related to its corrosion.

THE CONSEQUENCES OF CORROSION

The consequences of corrosion are many and varied and the effects of these on the safe,reliable and efficient operation of equipment or structures are often more serious than thesimple loss of a mass of metal. Failures of various kinds and the need for expensivereplacements may occur even though the amount of metal destroyed is quite small. Some ofthe major harmful effects of corrosion can be summarised as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structuralfailure or breakdown. When the metal is lost in localised zones so as to give a cracklikestructure, very considerable weakening may result from quite a small amount ofmetal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges,cars, aircraft).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when smallquantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm tothe surroundings. For example a leaky domestic radiator can

cause expensive damageto carpets and decorations, while corrosive sea water may enter the boilers of a powerstation if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These couldinclude frictional and bearing properties, ease of fluid flow over a pipe surface,electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosionproducts.
9. Added complexity and expense of equipment which needs to be designed to withstanda certain amount of corrosion, and to allow corroded components to be convenientlyreplaced.

CLASSIFICATION OF CORROSION:

General Corrosion:	**Localized Corrosion:**	**Metallurgically Influenced Corrosion:**	**Mechanically Assisted Degradation:**	**Environmentally Induced Cracking:**
Corrosive attack dominated by uniform thinning	High rates of metal penetration at specific sites	Affected by alloy chemistry & heat treatment	Corrosion with a mechanical component	Cracking produced by corrosion, in the presence of stress.
• Atmospheric corrosion • Galvanic corrosion • Stray-current corrosion • General biological corrosion • Molten salt corrosion • Corrosion in liquid metals • High – temperature corrosion	• Crevice corrosion • Filiform corrosion • Pitting corrosion • Localized biological corrosion	• Intergranular corrosion • Dealloying corrosion	• Erosion corrosion • Fretting corrosion • Cavitation and water drop impingement • Corrosion fatigue	• Stress – Corrosion Cracking (SCC) • Hydrogen Damage • Liquid metal embrittlement • Solid metal induced embrittlement

CORROSION PREVENTION

By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced. Thiscan be achieved in several ways:

1. Conditioning the Metal

This can be sub-divided into two main groups:

(a) Coating the metal, in order to interpose a corrosion resistant coating between metaland environment. The coating may consist of:

I. another metal, e.g. zinc or tin coatings on steel,

II. a protective coating derived from the metal itself, e.g. aluminium oxide on“anodised” aluminium,

III. organic coatings, such as resins, plastics, paints, enamel, oils and greases.

The action of protective coatings is often more complex than simply providing a barrierbetween metal and environment. Paints may contain a corrosion inhibitor zinc coating in iron or steel confers cathodic protection.

(b) Alloying the metal to produce a more corrosion resistant alloy, e.g. stainless steel, inwhich ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by aninvisibly thin, naturally formed film of chromium sesquioxide Cr2O3.

2. Conditioning the Corrosive Environment

(a) Removal of Oxygen

By the removal of oxygen from water systems in the pH range 6.5-8.5 one of the componentsrequired for corrosion would be absent. The removal of oxygen could be achieved by the useof strong reducing agents e.g. sulphite.

However, for open evaporative cooling systems this approach to corrosion prevention is notpractical since fresh oxygen from the atmosphere will have continual access.

(b) Corrosion Inhibitors

A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueousenvironment, reduces the rate of metal wastage. It can function in one of the following ways:

(i) anodic inhibitors – as the name implies an anodic inhibitor interferes with theanodic process.

$$Fe \rightarrow Fe^{++} + 2e^-$$

If an anodic inhibitor is not present at a concentration level sufficient to blockoff all the anodic sites, localised attack such as pitting corrosion can become aserious problem due to the oxidising nature of the inhibitor which raises themetal potential and encourages the anodic reaction (equation 1). Anodicinhibitors are thus classified as “dangerous inhibitors”. Other examples ofanodic inhibitors include orthophosphate, nitrite, ferricyanide and silicates.

(ii) cathodic inhibitors – the major cathodic reaction in cooling systems is thereduction of oxygen.

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$

There are other cathodic reactions and additives that suppress these reactionscalled cathodic inhibitors. They function by reducing the available area for thecathodic reaction. This is often achieved by precipitating an insoluble speciesonto the cathodic sites. Zinc ions are used as cathodic inhibitors because of theprecipitation of $Zn(OH)_2$ at cathodic sites as a consequence of the localised highpH.Cathodic inhibitors are classed as safe because they do

not cause localised corrosion.

(iii) adsorption type corrosion inhibitors– many organic inhibitors work by anadsorption mechanism. The resultant film of chemisorbed inhibitor is thenresponsible for protection either by physically blocking the surface from thecorrosion environment or by retarding the electrochemical processes. The mainfunctional groups capable of forming chemisorbed bonds with metal surfacesare amino ($-NH_2$), carboxyl ($-COOH$), and phosphonate ($-PO_3H_2$) althoughother functional groups or atoms can form co-ordinate bonds with metalsurfaces.

(iv) mixed inhibitors – because of the danger of pitting when using anodic inhibitorsalone, it became common practice to incorporate a cathodic inhibitor intoformulated performance was obtained by a combination of inhibitors than fromthe sum of the individual performances. This observation is generally referredto a ‘synergism’ and demonstrates the synergistic action which exists betweenzinc and chromate ions.

3. Electrochemical Control

Since corrosion is an electrochemical process its progress may be studied by measuring thechanges which occur in metal potential with time or with applied electrical currents.Conversely, the rate of corrosion reactions may be controlled by passing anodic or cathodiccurrents into the metal. If, for example, electrons are passed into the metal and reach themetal/electrolyte interface (a cathodic current) the anodic reaction will be stifled while thecathodic reaction rate increases. This process is called cathodic protection and can only beapplied if there is a suitable conducting medium such as earth or water through which acurrent can flow to the metal to be protected In most soils or natural waters corrosion of steelis prevented if the potential of the metal surface is lowered by 300 or 400 mV. Cathodicprotection may be achieved by using a DC power supply (impressed current) or by obtainingelectrons from the anodic dissolution of a metal low in the galvanic series such as aluminium,zinc or magnesium (sacrificial anodes). Similar protection is obtained when steel is coatedwith a layer of zinc. Even at scratches or cut edges where some bare metal is exposed thezinc is able to pass protective current through the thin layer of surface moisture.

In certain chemical environments it is sometimes possible to achieve anodic protection,passing a current which takes electrons out of the metal and raises its potential. Initially thisstimulates anodic corrosion, but in favourable circumstances this will be followed by theformation of a protective oxidised passive surface film.

Stress corrosion cracking

Stress corrosion cracking is cracking due to aprocess involving conjoint corrosion and strainingof a metal due to residual or applied stresses

Corrosion cantake many forms; the form that concerns us here is theinteraction of corrosion and mechanical stress to produce afailure by cracking. This type of failure is known as stresscorrosion cracking, often abbreviated to SCC

SCC is an insidious form of corrosion; it produces a markedloss of mechanical strength with little metal loss; the damageis not obvious to casual inspection and the stress corrosioncracks can trigger mechanical fast fracture and catastrophicfailure of components and structures.

SCC is not an inevitable process, and for most metals in mostenvironments it will not occur. We can therefore identifyspecific combinations of metal and environment that aresubject to the problem. Unfortunately, of course, as time goesby we identify more and more such combinations, especiallyas engineers strive to use materials more efficiently byincreasing working stresses and using less expensivematerials.

Heat Treatment

Heat Treatment is the controlled heating and cooling of metals to alter their physical andmechanical properties without changing the product shape. Heat treatment is sometimes doneinadvertently due to manufacturing processes that either heat or cool the metal such as weldingor forming. Heat Treatment is often associated with increasing the strength of material, but it canalso be used to alter certain manufacturability objectives such as improve machining, improveformability, restore ductility after a cold working operation. Thus it is a very enablingmanufacturing process that can not only help other manufacturing process, but can also improveproduct performance by increasing strength or other desirable characteristics.

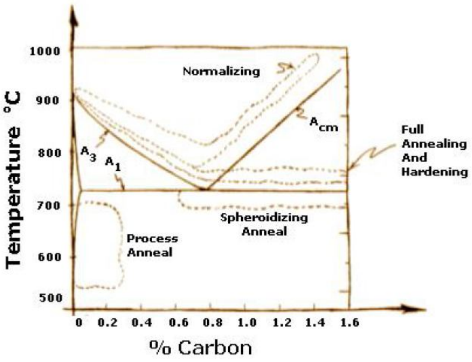
Steels are particularly suitable for heat treatment, since they respond well to heat treatment andthe commercial use of steels exceeds that of any other material. Steels are heat treated for one ofthe following reasons:

1. Softening
2. Hardening
3. Material modification

Softening: Softening is done to reduce strength or hardness, remove residual stresses, improvetoughness, restore ductility, refine grain size or change the electromagnetic properties of thesteel. Restoring ductility or removing residual stresses is a necessary operation when a largeamount of cold working is to be performed, such as in a cold-rolling operation or wiredrawing.Annealing — full Process, spheroidizing, normalizing and tempering austempering,martempering are the principal ways by which steel is softened.

Hardening: Hardening of steels is done to increase the strength and wear properties. One of thepre-requisites for hardening is sufficient carbon and alloy content. If there is sufficient Carboncontent then the steel can be directly hardened. Otherwise the surface of the part has to beCarbon enriched using some diffusion treatment hardening techniques.

Material Modification: Heat treatment is used to modify properties of materials in addition tohardening and softening. These processes modify the behavior of the steels in a beneficialmanner to maximize service life, e.g., stress relieving, or strength properties, e.g., cryogenictreatment, or some other desirable properties



HEAT TREATMENT PROCESS

Full annealing is the process of slowly raising the temperature about 50 °C (90 °F) above theAustenitic temperature line A3 or line ACM in the case of Hypoeutectoid steels (steels with <0.77% Carbon) and 50 °C (90 °F) into the Austenite-Cementite region in the case ofHypereutectoid steels (steels with > 0.77% Carbon).

It is held at this temperature for sufficient time for all the material to transform into Austenite orAustenite-Cementite as the case may be. It is then slowly cooled at the rate of about 20 °C/hr (36°F/hr) in a furnace to about 50 °C (90 °F) into the Ferrite-Cementite range. At this point, it can becooled in room temperature air with natural convection. The grain structure has coarse Pearlitewith ferrite or Cementite (depending on whether hypo or hyper eutectoid). The steel becomessoft and ductile.

Normalizing is the process of raising the temperature to over 60 ° C (108 °F), above line A3 orline ACM fully into the Austenite range. It is held at this temperature to fully convert the structureinto Austenite, and then removed form the furnace and cooled at room temperature under naturalconvection. This results in a grain structure of fine Pearlite with excess of Ferrite or Cementite.

The resulting material is soft; the degree of softness depends on the actual ambient conditions ofcooling. This process is considerably cheaper than full annealing since there is not the added costof controlled furnace cooling.

Process Annealing is used to treat work-hardened parts made out of low-Carbon steels (< 0.25%Carbon). This allows the parts to be soft enough to undergo further cold working withoutfracturing. Process annealing is done by raising the temperature to just below the Ferrite-Austenite region, line A1on the diagram. This temperature is about 727 ºC (1341 ºF) so heating itto about 700 ºC (1292 ºF) should suffice. This is held long enough to allow recrystallization ofthe ferrite phase, and then cooled in still air. Since the material stays in the same phase throughout the process, the only change that occurs is the size, shape and distribution of the grainstructure. This process is cheaper than either full annealing or normalizing since the material isnot heated to a very high temperature or cooled in a furnace.

Stress Relief Anneal is used to reduce residual stresses in large castings, welded parts and coldformedparts. Such parts tend to have stresses due to thermal cycling or work hardening. Partsare heated to temperatures of up to 600 - 650 ºC (1112 - 1202 ºF), and held for an extended time(about 1 hour or more) and then slowly cooled in still air.

Tempering is a process done subsequent to quench hardening. Quench-hardened parts are oftentoo brittle. This brittleness is caused by a predominance of Martensite. This brittleness isremoved by tempering. Tempering results in a desired combination of hardness, ductility,toughness, strength, and structural stability. Tempering is not to be confused with tempers onrolled stock-these tempers are an indication of the degree of cold work performed.

The mechanism of tempering depends on the steel and the tempering temperature. The prevalentMartensite is a somewhat unstable structure. When heated, the Carbon atoms diffuse fromMartensite to form a carbide precipitate and the concurrent formation of Ferrite and Cementite,which is the stable form. Tool steels for example, lose about 2 to 4 points of hardness on the

Rockwell C scale. Even though a little strength is sacrificed, toughness (as measured by impactstrength) is increased substantially. Springs and such parts need to be much tougher — these aretempered to a much lower hardness.

Tempering is done immediately after quench hardening. When the steel cools to about 40 ºC(104 ºF) after quenching, it is ready to be tempered. The part is reheated to a temperature of 150to 400 ºC (302 to 752 ºF). In this region a softer and tougher structure Troostite is formed.

Alternatively, the steel can be heated to a temperature of 400 to 700 ºC (752 to 1292 ºF) thatresults in a softer structure known as Sorbite. This has less strength than Troostite but moreductility and toughness.The heating for tempering is best done by immersing the parts in oil, for tempering upto 350 ºC(662 ºF) and then heating the oil with the parts to the appropriate temperature. Heating in a bathalso ensures that the entire part has the same temperature and will undergo the same tempering.For temperatures above 350 ºC (662 ºF) it is best to use a bath of nitrate salts. The salt baths canbe heated upto 625 ºC (1157 ºF). Regardless of the bath, gradual heating is important to avoidcracking the steel. After reaching the desired temperature, the parts are held at that temperaturefor about 2 hours, then removed from the bath and cooled in still air.

Hardening

Hardness is a function of the Carbon content of the steel. Hardening of a steel requires a changein structure from the body-centered cubic structure found at room temperature to the facecenteredcubic structure found in the Austenitic region. The steel is heated to Autenitic region.When suddenly quenched, the Martensite is formed. This is a very strong and brittle structure.When slowly quenched it would form Austenite and Pearlite which is a partly hard and partlysoft structure. When the cooling rate is extremely slow then it would be mostly Pearlite which isextremely soft.

Usually when hot steel is quenched, most of the cooling happens at the surface, as does thehardening. This propagates into the depth of the material. Alloying helps in the hardening and bydetermining the right alloy one can achieve the desired properties for the particular application.


AUSTENITE


MARTENSITE


CEMENTITE


PEARLITE
COARSE


PEARLITE
FINE

ALUMINIUM ALLOYS

- WROUGHT ALUMINIUM ALLOYS
    - Al–Zn–Mg–Cu superalloys and high-strength alloys
    - Long-life aluminium alloys
    - High-workable weldable corrosion-resistant aluminium alloys
    - Al-Li alloys with lowered density
    - Heat-resistant alloys
    - SiAl-type laminates

CASTABLE ALUMINIUM ALLOYS

- High strength castablealuminium alloys
- Castable heat-resistant aluminium alloys
- Weldable corrosion-resistant aluminium alloys

TITANIUM ALLOYS

- WROUGHT TITANIUM ALLOYS
    - Heat-resistant titanium alloys for GTE components
    - Structural titanium alloys
    - High strength structural titanium alloys
    - Intermetallic titanium alloys
- CASTABLE TITANIUM ALLOYS

- **MAGNESIUM ALLOYS**
  - WROUGHT MAGNESIUM ALLOYS
    - Medium-strength alloys
    - High-strength alloys
    - Granulated alloys
    - Heat-resistant alloy
    - Ultra-light alloys (alloys with lowered density)
  - CASTABLE MAGNESIUM ALLOYS
    - Mg–Zn–ZrhHigh-strength alloys
    - Mg–Al–Zn corrosion-resistant alloys
    - Mg–REM–Zr heat-resistant alloys
    - Antiburning-on adding materials

  Magnetic alloys and intermetallics are metallic materials capable of producing a constant magnetic field for a prolonged period of time. There are only a limited number of chemical elements that can produce alloys with permanent magnetic properties at ambient temperature; Fe, Ni, Co and rare earth metals are the most important ones.

  1. Samarium-Cobalt Alloys
  2. Aluminium-Nickel-Cobalt Alloys
  3. Neodymium-Iron-Boron Alloys

Effects of Alloying Elements in Steel

Alloying elements are added to effect changes in the properties of steels. The basis of thissection is to cover some of the different alloying elements added to the basic system ofiron and carbon, and what they do to change the properties or effectiveness of steel.

Carbon

As I've already stated, the presence of carbon in iron is necessary to make steel. Carbon isessential to the formation of cementite (as well as other carbides), and to the formation ofpearlite, spheroidite, bainite, and iron-carbon martensite, with martensite being thehardest of the micro-structures, and the structure sought after by knifemakers. Thehardness of steel (or more accurately, the hardenability) is increased by the addition ofmore carbon, up to about 0.65 percent. Wear resistance can be increased in amounts up toabout 1.5 percent. Beyond this amount, increases of carbon reduce toughness andincrease brittleness. The steels of interest to knifemakers generally contain between 0.5and 1.5 percent carbon. They are described as follows:

- Low Carbon: Under 0.4 percent
- Medium Carbon: 0.4 - 0.6 percent
- High Carbon: 0.7 - 1.5 percent

Carbon is the single most important alloying element in steel.

Chromium

As with manganese, chromium has a tendency to increase hardness penetration. Thiselement has many interesting effects on steel. When 5 percent chromium or more is usedin conjunction with manganese, the critical quenching speed is reduced to the point thatthe steel becomes air hardening. Chromium can also increase the toughness of steel, aswell as the wear resistance. Probably one of the most well known effects of chromium onsteel is the tendency to resist staining and corrosion. Steels with 14 percent or morechromium are referred to as stainless steels. A more accurate term would be stainresistant. Stainless tool steels will in fact darken and rust, just not as readily as the non-stainlessvarieties. Steels with chromium also have higher critical temperatures in heattreatment.

Nickel

Nickel increases the strength of ferrite, therefore increasing the strength of the steel. It isused in low alloy steels to increase toughness and hardenability. Nickel also tends to helpreduce distortion and cracking during the quenching phase of heat treatment.

Molybdenum

Molybdenum increases the hardness penetration of steel, slows the critical quenchingspeed, and increases high temperature tensile strength.

Vanadium

Vanadium helps control grain growth during heat treatment. By inhibiting grain growth ithelps increase the toughness and strength of the steel.

Tungsten

Used in small amounts, tungsten combines with the free carbides in steel during heattreatment, to produce high wear resistance with little or no loss of toughness. Highamounts combined with chromium gives steel a property known as red hardness. Thismeans that the steel will not lose its working hardness at high temperatures. An exampleof this would be tools designed to cut hard materials at high speeds, where the frictionbetween the tool and the material would generate high temperatures.

Copper

The addition of copper in amounts of 0.2 to 0.5 percent primarily improves steelsresistance to atmospheric corrosion. It should be noted that with respect to knife steels,copper has a detrimental effect to surface quality and to hot-working behavior due tomigration into the grain boundaries of the steel.

Niobium

In low carbon alloy steels Niobium lowers the transition temperature and aids in a finegrain structure. Niobium retards tempering and can decrease the hardenability of steelbecause it forms very stable carbides. This can mean a reduction in the amount of carbondissolved into the austenite during heat treating.

Boron

Boron can significantly increase the hardenability of steel without loss of ductility. Itseffectiveness is most noticeable at lower carbon levels. The addition of boron is usuallyin very small amounts ranging from 0.0005 to 0.003 percent.

Titanium

This element, when used in conjunction with Boron, increases the effectiveness of the

Boron in the hardenability of steel.