Aluminium and Corrosion

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Introduction

Although aluminium is a very reactive metal with a high affinity for oxygen, the metal is highly resistant to most environments and to a great variety of chemical agents. This resistance is due to the inert and protective character of the aluminium oxide film which forms on the metal surface. In most environments, the rate of corrosion of aluminium decreases rapidly with time. In only a few cases, e.g. caustic soda, does the corrosion rate approximate to the linear.

Although the oxide film is extremely thin, between 50 and 100 Angstroms, it forms a protective barrier between the metal and the surrounding medium as soon as the metal comes into contact with an oxidising environment, such as water. The physical-chemical stability of the oxide film determines the corrosion resistance of the aluminium. This stability is dependent upon the pH value of the environment, since the oxide film is stable within the pH range of about 4 to 8. Below and above these values, acid dissolution yields Al^{3+} ions and the alkaline dissolution leads to the formation of $Al(OH)_4$ ions.
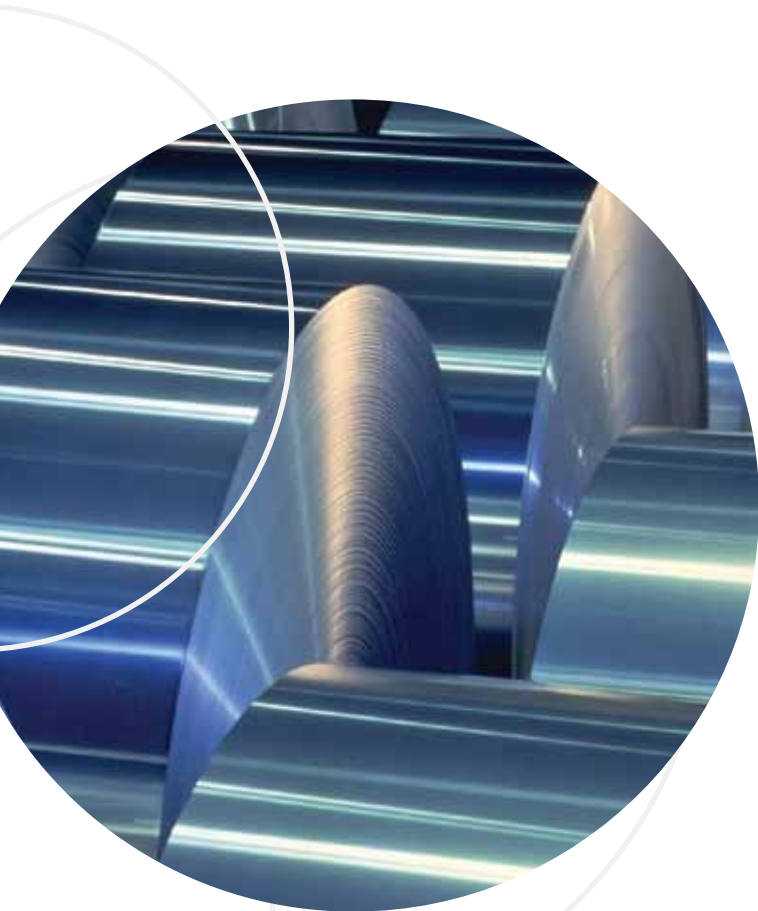
Electrochemical Aspects of Corrosion

Reactions

Any corrosion reaction in aqueous solution must involve oxidation (anodic reaction) of the metal and reduction (cathodic reaction) of a species in solution, with consequent electron transfer between the two reactants. The anodic and cathodic reactions occur at the same rate and simultaneously upon a metal's surface, therefore the metal is electrically charged, and thus the rate of oxidation is equal to the rate of reduction. For example in this situation, the corrosion of aluminium in water may be represented by the two half reactions:-

Oxidation (anodic reaction) $Al => Al^{3+} + 3e$

Reduction (cathodic reaction) $H^+ + e => \frac{1}{2} H_2$

Uniform Attack

This is a common form of corrosion, where all areas of the metal corrode at a similar rate. Over a period of time, the exposed metal undergoes oxidation by aggressive ions (such as chloride ions), until the metal fails, due to thinning. Uniform attack can be predicted on the basis of immersion tests, e.g. weight loss over a period of time. It can be prevented in several ways as described below:-

Selection of appropriate materials and/or coatings, non-metallic or metallic e.g. anodising.

Use of inhibitors, such as chromic acid in the case of aluminium alloys.

Application of cathodic protection, such as sacrificial zinc anodes.

Galvanic Corrosion

This type of corrosion occurs when two conducting materials of different chemical composition are joined and exposed to a conducting solution e.g. when iron is connected to copper in water. Iron passes into solution as Fe^{2+} ions and the residual electrons are conducted through to the copper and, as a consequence, hydroxyl ions, 0H- , are formed at the surface. Galvanic corrosion is very damaging because it concentrates on the less noble metal at the metal-metal junction, where deep attack occurs. At the junction a large corrosion current can pass because the electrical resistance of the short path through the electrolyte is low.

Common forms of metal joining, e.g. brazing, welding etc. provide junctions at which galvanic

corrosion can develop. Galvanic corrosion on a microscopic scale can also occur between constituents of multi-phase alloys and of impure metals which contain foreign particles and intermetallic compounds.

When aluminium is coupled with copper or brass, corrosive attack upon the aluminium is accelerated by these materials in severe or modest atmospheres and conditions of immersion. Contact between aluminium and stainless steel (18/8, 18/8/2 and 13% Cr) will only slightly increase the corrosion of the aluminium in dry atmospheres. However, it is markedly increased in moist atmospheres, particularly in marine conditions.

A simple way of avoiding bimetallic corrosion is to isolate the two metals from one another. This can be achieved by good design and where necessary by inserting an insulating material such as neoprene between the metal/metal contact. This would be important in an application where an aluminium component is fixed in place with a steel article.

Crevice Corrosion

Intense localised corrosion, ranging from small pits to extensive corrosion over the whole surface, can occur within narrow crevices that may be formed by:-

The geometry of the structure, e.g. riveted plates, threaded joints etc.

Contact of metal with non-metallic solids, e.g. plastics, rubber etc.

Deposits of sand, dirt or permeable corrosion products on the metal surface.

Differential aeration plays an important part in the mechanism of crevice corrosion, but it is not the sole cause. The situation in reality is far more complex, owing to the formation of acid within the crevice.

In an aluminium crevice, corrosion makes little progress, probably due to the precipitation of aluminium oxide, a corrosion product that restricts the entrance to the recess.

Pitting

Pitting is a form of localised corrosion that proceeds because of local cell action that produces cavities at the surface. These cavities may become filled with corrosion products. Corrosion products can form caps over pit cavities, which are described as nodules. While the shapes of the pits vary widely, they usually are roughly saucer shaped, conical, or hemispherical. Pit walls usually are irregular in profile when viewed under a microscope.

Pitting occurs when a film-protected metal is almost, but not completely, resistant to corrosion, as in the case of aluminium and its alloys. It usually occurs on a metal surface immersed in a solution or moist environment, such as soil. It can occur on a surface exposed to the atmosphere if there are droplets of moisture or condensed moisture film present on the metal surface. Pitting may also occur in crevices, in which case it is called crevice corrosion (see above).

Pitting usually occurs on metals that are covered with a very thin, often transparent, passive oxide film that may form during fabrication or be produced by reaction with the environment. Thus, pitting occurs on magnesium, aluminium, titanium, stainless steel, and copper in cases in which surface films develop. Pits initiate at flaws within the surface film and at sites where the film is damaged mechanically under conditions in which self-repair will not occur. Most cases of pitting are believed to be caused by local cathodic sites in an otherwise normal surface.

If a pitted surface is dried out, the pits will terminate. When rewetted, some of the pits may be reactivated. This may be due to the re-establishment of the conditions or to differential aeration between the solution in the main pit cavity and solutions in some of the cracks that emanate from it deeper into the metal.

Thermodynamically, aluminium is capable of reacting with a wide range of chemical substances. Free energy considerations make the reactions with oxygen and water particularly favourable. However, aluminium shows a high resistance to reactions which would result in corrosion in most neutral solutions. This is generally accepted to be due to the rapid growth of oxide films or absorbed oxygen on its surface. The oxide film forms within seconds, is self-healing, has a slow thickening rate and is very compact and adherent. Thus, this acts as a barrier between the metal surfaces, whereas, in crevice corrosion, attack is due to the shielding of a small area of surface from the bulk solution.

Intergranular Corrosion

This form of corrosion consists of localised attack in which a path is corroded preferentially along the grain boundaries of the metal. The mechanism is electrochemical and is dependent upon the formation of local cells at the grain boundaries. The local cells are a result of second phase precipitates

at the grain boundaries. During the formation of intermetallic second phase precipitates along the grain boundaries, an adjacent matrix zone is formed that has a different solution potential. The precipitate may be anodic to the matrix such as Mg_5Al_8, in which case it corrodes preferentially; or it may be cathodic, such as $CuAl_2$, in which case it does not corrode, but stimulates corrosion in the adjacent matrix zone. In either case, selective grain boundary corrosion occurs. The degree of susceptibility of an alloy to intergranular attack can vary depending on its microstructure, in particular, the amount, size, and distribution of second phases, which is a result of the metallurgical history and thermal treatment. Heat treatments that cause precipitation throughout the grain tend to diminish the intergranular attack. It is significant that in certain aged conditions, Al-Mg-Cu alloys may suffer intergranular corrosion, but not stress corrosion cracking, as a result of different precipitate distribution.

Exfoliation Corrosion

Exfoliation corrosion is a specific type of selective attack that proceeds along multiple narrow paths e.g. grain boundaries which run parallel to the surface of a metal. Generation of corrosion products forces the layers apart and causes the metal to 'swell'. Metal flakes may be pushed up and even peel from the metal surface. Exfoliation corrosion is most common in the heat treatable Al-Mg-Cu and Al-Zn-Mg-Cu alloys. This form of corrosion is associated with a marked directionality of the grain structure. Applied stresses are not necessary for exfoliation to occur. However, in alloys susceptible to stress corrosion cracking, the corrosion product wedging action undoubtedly contributes to the propagation of the exfoliation attack. It is important to note that some alloys not susceptible to stress corrosion cracking (Al-Mg-Si) may suffer exfoliation corrosion. However, if the grain structure is equiaxed, exfoliation corrosion does not usually occur.

Stress Corrosion Cracking

Stress Corrosion Cracking, SCC, is a term given to the intergranular or transgranular cracking of a metal by the combined action of a static tensile stress and a specific environment.

SCC can occur unexpectedly, resulting in the failure of components. Often a material, chosen for its corrosion resistance in a given environment, is found to fail at a stress level well below its normal fracture stress. Rarely is there any obvious evidence of an impending failure, and it can occur in components which are externally unstressed.

It is generally agreed that there is no single mechanism for SCC. Any combination of a number of significant factors may contribute to a given SCC failure.

Corrosion Fatigue

Under conditions of simultaneous cyclic stressing and corrosion, the reduction in strength is greater than the additive effects of the separate processes. Although it is often possible to provide adequate protection for metallic parts which are stressed under static conditions, most surface films, including naturally protective oxides, can be more easily broken or disrupted under cyclic loading.

In general, the fatigue strength of a material in a particular corrosive medium can be related to the corrosion resistance of the materials in that medium. Under conditions of corrosion fatigue, all types of aluminium alloys exhibit about the same percentage reduction in strength when compared with their fatigue strength in air. When tested in sodium chloride solutions, the fatigue strength at 108 cycles is normally between 25% and 35% of that in air. Also the corrosion-fatigue strength of a particular aluminium alloy can appear to be virtually independent of its metallurgical condition.

Filiform Corrosion

This appears as a random non-branching white tunnel of corrosion product, either on the surface of non-protected metal or beneath surface coatings. It is a structurally insensitive form of corrosion which is often more detrimental to appearance than strength, although thin foil may be perforated, and attack of thin clad sheet, as used in aircraft construction, may expose the less corrosion-resistant aluminium alloy core.

Alloy Selection

Wrought Alloys

The durability of aluminium enables its use in many applications and in doing so it may come into contact with aggressive environments. To achieve strength, aluminium is alloyed with other elements. Not only are the mechanical properties affected, but also the corrosion properties change.

The common groups of wrought alloys are shown below;

1XXX Commercially pure Aluminium.

2XXX Aluminium-copper.

3XXX Aluminium-manganese.

5XXX Aluminium-magnesium.

6XXX Aluminium-magnesium-silicon.

7XXX Aluminium-zinc-magnesium.

The corrosion resistance of the 1XXX series is excellent, and this leads to a wide application in the packaging industry where it is used for foils. The combined corrosion resistance and ductility makes this material a superb choice for cooking utensils.

The aluminium-copper alloys of the 2XXX series are very strong and are therefore used for structural purposes, but the additional strength achieved is at the detriment of their durability. These alloys are significantly affected in heavily polluted industrial or marine environments. Therefore this group of alloys requires protection in aggressive environments.

The 3XXX series alloys are most commonly used in sheet form and the control of mechanical properties is achieved by cold work and annealing. The alloys are used in general engineering and packaging, particularly closures and cans, where deep drawing is used. They have good corrosion resistance but in aggressive environments they may be lacquered or painted.

The 5XXX series have even better corrosion resistance than the 6XXX series. Unlike the 6XXX series, the 5XXX series can be used in marine conditions where total immersion in sea water is required.

The 6XXX series alloys are the most common amongst aluminium alloys and are widely used in transport, engineering and architecture. The good corrosion resistance of these alloys means that they can be used in marine and industrial environments.

The 7XXX series are high-strength alloys and thus may have reduced corrosion resistance. Hence there is a need for protection in aggressive environments to prevent, for example, stress corrosion cracking.

Casting Alloys

Aluminium casting alloys are still commonly specified as the LM series from the former BS 1490. As the current standard is now BS EN 1676, with a five-figure designation, the information below refers to the LM series, but with a BS EN 1676 equivalent in brackets.

Most aluminium casting alloys are classified as having good corrosion resistance, and if used for purposes involving exposure out-of-doors, they will suffer no appreciable loss of strength as a result of corrosion. Weathering tests lasting more than ten years, carried out by The Association of Light Alloy Refiners, confirm that there is little difference in the resistance to atmospheric attack of the casting alloys LM2 (EN 46100), LM4 (EN 45200), LM5 (EN 51300), LM6 (EN 44100), LM21 (EN 45000) and LM24 (EN 46500). Under normal weathering conditions, superficial attack and the surface appearance of the castings are more influenced by the particular atmospheric conditions of the exposure site than by the differences in composition between the alloys. It is recommended that casting alloys such as LM22 (EN 45400), LM26, LM30 and LM12 be protected by painting if used under conditions involving exposure to the weather.

For more aggressive environments, e.g. marine applications or in the manufacture of food or chemicals, LM5 (EN 51300), LM6 (EN 44100), LM9 (EN 43100), LM20 (EN 47000), LM25 (EN 42000) and LM31 (EN 71000) will generally be found to be superior to the other casting alloys. LM6 has many other advantages, but LM5 is particularly recommended where it is necessary that a bright surface be maintained. LM0 (99.5% aluminium) has the best resistance to corrosion of all the casting alloys and may be used where the softness and low strength are not a disadvantage. It is however difficult to cast, except in the simplest of shapes.

Corrosion Protection

A variety of protection methods are applied to aluminium and its alloys to enhance their corrosion resistance. Amongst the most common methods is anodising. This is an electrolytic process which

produces a hard, relatively thick film of aluminium oxide on the surface of the aluminium when the metal is made the anode in a suitable electrolyte and current is passed through the circuit. The different types of anodising used commercially are:-

Sulphuric Acid Anodising.

Integral Colour Anodising.

Chromic Acid Anodising.

Hard Anodising.

Other protection methods include chemical conversion coatings and various paint finishes e.g. powder coating. Chemical pre-treatment prior to painting is essential. Sacrificial anodes, e.g. zinc, can be used to protect aluminium alloy structures when used in marine environments.

Further information about aluminium and aluminium alloys, their production, fabrication and end use can be obtained from:

(1) European Aluminium Association in Brussels
   www.eaa.net

(2) International Aluminium Institute in London
   www.world-aluminium.org