CHAPTER 1

Introduction: Aluminium, Its Properties, Alloys and Finishes

1. HISTORY, PROPERTIES AND ALLOYS

The history of the light metal industry, as that of many other industries in this century, is one of notable and ever accelerating expansion and development. There are few people today who are not familiar with at least some modern application of aluminium and its alloys. The part it plays in our everyday life is such that it is difficult to realise that a century ago the metal was still a comparative rarity.

The excellent corrosion resistance of pure aluminium is largely due to its affinity for oxygen; this results in the production of a very thin but tenacious oxide film which covers the surface as soon as a freshly-cut piece of the metal is exposed to the atmosphere. This oxide coating is of great significance in the production of practically every type of surface finish for the metal. It is, of course, the basis of what is probably the most corrosion-resistant finish of all, namely, that group of finishes which involves the technique of anodic oxidation in its varied forms. Here, the natural film is, in effect, greatly thickened and strengthened by electrochemical means.

On the other hand, the tenacity of the natural oxide film is a serious adverse factor in the production of other finishes, such as those based on electrodeposition, and also, but to a lesser extent, the organic finishes, as it must be removed or transformed before the alternative coating can be successfully applied. Special techniques have had to be evolved to effect this.

History of aluminium

Aluminium is a strongly electro-negative metal and possesses a strong affinity for oxygen; this is apparent from the high heat of formation of its oxide. For this reason, although it is among the six most widely distributed metals on the surface of the earth, it was not isolated until well into the nineteenth century.

Alumina (Al_2O_3) was known, however, in the eighteenth century, and the first unsuccessful attempts to isolate the metal were made by Sir Humphry Davy in 1807, when the isolation of the alkali metals had made a powerful reducing agent available. It was not, however, until 1825 that the Danish Worker, H.C. Oersted, succeeded in preparing aluminium powder by the reduction of anhydrous aluminium chloride with sodium amalgam; two years later, F. Wohler replaced the amalgam by potassium, and between 1827 and 1847 discovered and listed many of the chemical and physical properties. However, many years passed before the metal could be produced commercially.

The father of the light metal industry was probably the French scientist, Henri Sainte-Claire Deville, who in 1850 improved Wohler's method of preparation by replacing potassium by sodium, and by using the double chloride of sodium and aluminium as his source of the metal, thus making the production of aluminium a commercial proposition; the price of the metal, however, was still comparable with that of gold.

The production of aluminium received a further impetus when Robert Bunsen and, following him, Deville, showed how the metal could be produced electrolytically from its ores.

In 1885, the brothers Cowle produced the first aluminium alloys containing iron and copper, soon after which the invention of the dynámo made a cheaper supply of electricity available and resulted, in 1886, in Héroult's and Hall's independent French and American patents for the electrolytic production of aluminium from alumina and molten cryolite (AlF_3NaF). Thenceforth, the production of aluminium in Europe centred round the first factory in Neuhausen, while Hall's process was applied in the U.S.A. in Pittsburgh. Modern production of aluminium begins from the mineral bauxite, which contains approximately 25% of aluminium. This is converted to alumina by digestion with a solution of sodium hydroxide under pressure (the Bayer process), and the purified alumina produced is added to a molten mixture of cryolite and fluorspar. This mixture is electrolysed in a cell with carbon anodes (Fig. 1-1) and the molten mixture is tapped from the bottom of the cell.

Properties of aluminium

The three main properties on which the application of aluminium is based are its low density of approximately 2.7, the high mechanical strength achieved

Fig. 1-1.   Modern pot line at the British Alcan smelter at Lynemouth

by suitable alloying and heat treatments, and the relatively high corrosion resistance of the pure metal. Other valuable properties include its high thermal and electrical conductance, its reflectivity, its high ductility and resultant low working cost, its magnetic neutrality, high scrap-value, and the non-poisonous and colourless nature of its corrosion products which facilitates its use in the chemical and food-processing industries. Still further valuable features are obtained by various treatments of the metal; these will be considered when the applications of aluminium and its finishes are considered.

In its pure state, aluminium is, however, a relatively soft metal with a yield strength of only 34.5 N/mm² (5,000 lb/in²) and a tensile strength of 90 N/mm² (13,000 lb/in²). Through the development of a wide range of alloys, however, very varied strengths and ductility can be achieved, and this has led to the many applications of today. For example these range from the use of very thin foil material in the packaging industry, ductile materials for drink containers, and highly conductive alloys for electrical purposes, to relatively low-strength alloys for the building industry and high strength materials for aircraft and armoured vehicles.

The metal in its pure state has a relatively high corrosion resistance and needs less protection than most metals. On the other hand, the commercial metal and its alloys, though resistant, are distinctly more sensitive to corrosion, and the
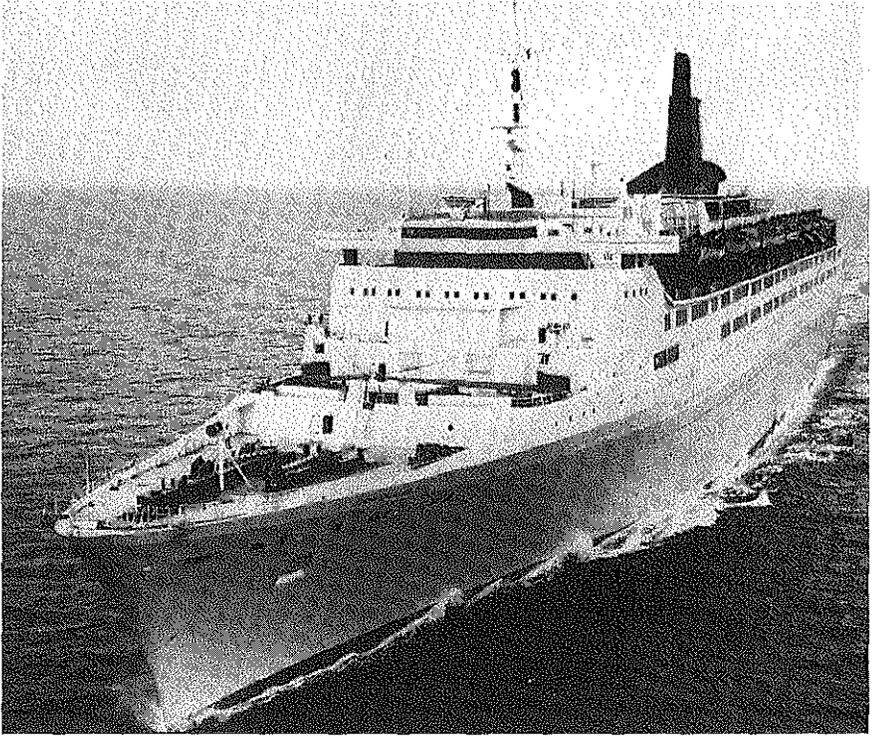
Fig. 1-2. The Queen Elizabeth 2, which incorporates 1000 tons of 5083 alloy plate and extrusions

[Courtesy Cunard Line]

development of high strength light alloys, containing quantities of heavy metals such as copper, zinc or nickel, has heightened the need for protective surface treatments. The nature of the heavy metal additions appreciably influences the alloy's susceptibility to corrosion, and high mechanical strength and corrosion resistance have so far proved largely incompatible. The development of satisfactory protective finishes for these metals has been, therefore, of very great importance.

Brief consideration is now given to the properties of the various aluminium alloys which are available in relation both to their corrosion resistance and applications.

Development of aluminium alloys

The chief alloying constituents added to aluminium are copper, magnesium, silicon, manganese, nickel and zinc. All of these are used to increase the strength of pure aluminium.

Two classes of alloys may be considered. The first are the 'cast alloys' which are cast directly into their desired forms by one of three methods (i.e., sand-casting, gravity die casting or pressure die casting), while the second class, the 'wrought alloys', are cast in ingots or billets and hot and cold worked mechanically into extrusions, forgings, sheet, foil, tube and wire. The main classes of alloys are the 2000 series (Al-Cu alloys), which are high-strength materials used mainly in the aircraft industry, the 3000 series (Al-Mn alloys) used mainly in the canning industry, the 5000 series (Al-Mg alloys) which are used unprotected for structural and architectural applications, the 6000 series (Al-Mg-Si alloys) which are the most common extrusion alloys and are used particularly in the building industry, and the 7000 series (Al-Zn-Mg alloys) which are again high strength alloys for aircraft and military vehicle applications.

The alloy used in any particular application will depend on factors such as the mechanical and physical properties required, the material cost and the service environment involved. If a finishing treatment is to be applied, then the suitability of the alloy for producing the particular finish desired will be an additional factor to be taken into account. The great benefit of aluminium is that such a wide variety of alloys with differing mechanical and protection properties is available, and these, together with the exceptional range of finishes which can be used, make aluminium a very versatile material.

2. THE OXIDE FILM

When a freshly formed aluminium metal surface is exposed to the atmosphere, it is immediately covered with a thin film of oxide, and this oxide film quickly re-forms when damaged. An important and beneficial feature of this oxide film is that its molecular volume is stoichiometrically 1.5 times that of the metal used up in oxidation. This then means that the oxide film is under compressive stress, and will not only cover the metal continuously, but can cope with a certain amount of substrate deformation without rupturing. It is to this protective surface layer that the aluminium industry owes its existence.

Reports of the structure of this low temperature, air-formed film have varied widely although, in general, it is assumed to be amorphous, with the outer surface being a hydrated aluminium oxide. At higher temperatures (above 450°C), crystalline γ-Al_2O_3 is formed, and then, in the molten state, α-Al_2O_3 can occur.

The kinetics of oxide growth on pure aluminium are complex. The currently accepted mechanism has been described recently by Wefers.[1] At ambient temperatures a limiting oxide film thickness of 2 to 3 nm will be produced within one day; thermal oxidation is controlled by diffusion of aluminium and oxygen ions at temperatures up to $\sim 400°C$ and, in this temperature range, asymptotically decaying rate laws are observed. However, when the temperature

Fig. 1-3.   The twin bascule bridge at Hendon Junction, Sunderland, Co.
Durham – the world's first all-aluminium structure of this type

is raised towards and above 450°C, the exponential oxidation rate changes to a
linear relationship between weight gain and time. This change in mechanism
represents crystallisation to γ-Al_2O_3, which will disrupt the continuity of the
film. At temperatures above 500°C, it has been reported[2] that the preparation of
the sheet, i.e. both metallurgical and surface roughness features, can alter the
oxidation kinetics.

TABLE 1-1

Thickness of oxide coatings on aluminium

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Natural oxide film on pure Al or Al-Mg alloy (formed at below 300°C)	1-3 nm
Natural oxide film on pure Al (formed at temperatures above 300°C)	up to 30 nm
Natural oxide film on Al-Mg alloy (formed at temperatures above 300°)	up to 3,000 nm (3 µm) (depending on temp. and bulk Mg content)
Normal chemical oxide coating (e.g. M.V.V., Alrok, etc.)	2.5-5 µm (2,500-5,000 nm)
Normal barrier layer anodizing	0.25-0.75 µm (250-750 nm)
Normal protective anodic coating (e.g. sulphuric acid anodizing)	5-30 µm (5,000-30,000 nm)
Hard anodic coatings (e.g. for engineering purposes)	25-150µm (25,000-150,000 nm)
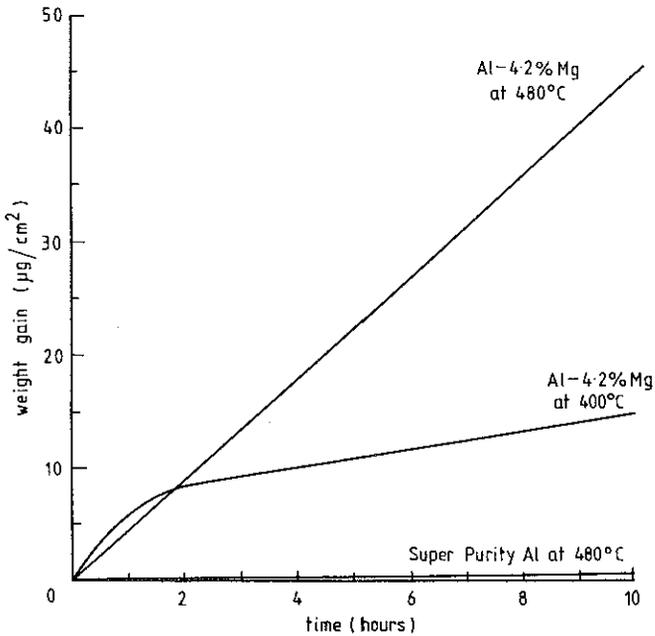
Fig. 1-4. A comparison of weight gain curves for oxidation under dry conditions[4]

The major alloying element incorporated within the oxide film is magnesium. At temperatures above 340°C,[3] magnesium diffuses from the bulk of the alloy and, even at levels less than 50 ppm magnesium, there is a competitive oxidation reaction between magnesium diffusion outwards and oxygen diffusion inwards. At higher levels of bulk magnesium (up to 4%), a duplex film of aluminium oxide close to the metal, and an outer layer of MgO, results. These oxide films will thicken until the bulk magnesium level is depleted. Typical weight gain curves for Al-4.2%Mg, as compared to super-purity aluminium, are shown in Fig. 1-4.[4] The current understanding of oxidation of aluminium-magnesium alloys is summarised by Wefers[1] and Field et al.[5]

Table 1-1 indicates the thickness of typical natural oxide coatings in comparison with chemical and anodic oxidation coatings.

Breakdown of the oxide film can result from mechanical rupture, or from chemical attack by anions such as chloride ions. In most cases repair is instantaneous and, depending on the moisture content of the environment, can either be accompanied by the oxygen reduction reaction or the hydrogen evolution reaction shown overleaf:

$$4Al - 12e^- \rightarrow 4Al^{3+}$$
$$3O_2 + 12e^- \rightarrow 6O^{2-}$$

anodic

cathodic

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
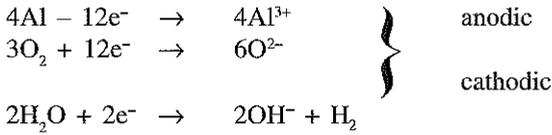
In the first cathodic reaction aluminium oxide results, whereas in the second, hydroxide is formed.

There is growing evidence that flaws pre-exist in the oxide film, and can act as nucleation sites for film breakdown. Information has been gained both from electrochemical studies[6,7] and transmission electron microscopy.[8] It is proposed that, in solution, flaws are continually being developed and repassivated, and the presence of aggressive ions hinders the repassivation step, allowing pits to nucleate. Electrochemical noise generated prior to pit initiation provides strong evidence for this type of process. However, even with the existence of flaws, the aggressive ions would still have to penetrate the flaw bases. This could be by the formation of short-lived complex ions or by the development of islands of salts, e.g. $AlCl_3.6H_2O$, followed by currentless dissolution.[9] Alternatively, the local pH in the flaw may become sufficiently low to effectively defilm the base of the flaw and expose the aluminium. The latter mechanism is favoured at present. The result of film breakdown is corrosion and this is considered in the next section.

3. CORROSION OF ALUMINIUM

Whilst aluminium and its alloys generally have good corrosion resistance, localised forms of corrosion can occur, and it is important to understand the factors contributing to these forms of corrosion.

Corrosion may be defined as the reaction between a metal and its immediate environment, which can be natural or chemical in origin. The most recognisable form of corrosion is, perhaps, the rusting of iron. All metals react with natural environments but the extent to which this happens can vary; for noble metals like gold the amount is insignificant whereas for iron it is considerable. Aluminium is no exception but, fortunately, it has the propensity of self passivation and for many applications corrosion is not a problem.

Factors contributing to corrosion

There are two main factors which influence the general corrosion behaviour of aluminium; one is the type and aggressiveness of the environment and the

second is that of its chemical and metallurgical structure. Environments can vary from outdoor atmospheres to media such as soils, waters, building materials, food and chemicals etc. Outdoor atmospheres are usually classified as either rural, industrial or marine depending on their location. In rural atmospheres the degree of natural pollution is usually low, but industrial and marine environments are more aggressive, usually due to the presence of sulphates and chlorides respectively. Soils, waters and building materials vary in aggressiveness depending on such properties as composition, chemical activity, degree of aeration and electrical conductivity. Chemical environments usually have unique compositions and their corrosive effects can be fairly accurately determined.

Pure aluminium displays the highest corrosion resistance, but as purity decreases and alloying elements are added this resistance decreases.[10] Copper lowers resistance more than other elements, whilst magnesium has the least effect. The influence of the main alloying elements and impurities on the corrosion resistance of aluminium is summarised in Table 1-2.

TABLE 1-2

General effect of major alloying elements on the corrosion resistance of aluminium

Element	Effect			
	Marked	Moderate	Slight	V. Slight
Copper	✓			
Magnesium				✓
Zinc				✓
Silicon			✓	
Manganese				✓
Chromium				✓
Zirconium				✓
Titanium				✓
Iron + Silicon		✓		

The metallurgical state of an aluminium alloy for a given composition is determined by its fabrication history. In the wrought form it will be made either by the procedure of work-hardening or by that of solution heat-treatment. Aluminium alloys are also available in the cast form. Briefly, work-hardening involves deformation at room or slightly elevated temperatures, and for semi-fabricated products the process used is that of rolling. The main features resulting from rolling are dislocations, in arrays varying from subgrains with ragged boundaries, to high density configurations of 'forests' and slip bands; Fig. 1-5
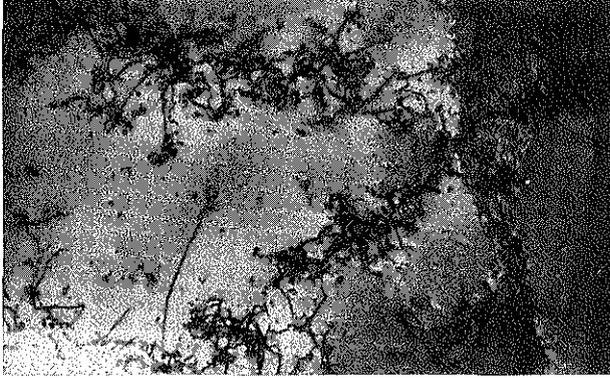
Fig. 1-5. 'Ragged' sub-grain boundaries resulting from small amounts of cold rolling (Al-Mg alloy) (210,000)

illustrates some of these. Cold worked structures also arise from processes such as shearing, stamping and forming. The two main work-hardening alloy groups are those based on Al-Mn (3000 series) and on Al-Mg (5000 series).

In general terms solution heat-treatment consists of two basic stages. The first involves soaking at temperatures between 450°C and 550°C for predetermined periods depending on the particular alloy composition, followed by quenching either into water or into air, again depending on the alloy. The second stage is that of ageing, which is carried out at temperatures between 20°C and about 175°C. During the first stage most of the alloying elements are taken into solid solution and then partly released from this state during ageing. Except at grain boundaries and other energetically favourable regions, material released from solid solution remains coherent with the matrix and by so doing increases strength. If the ageing period is prolonged or the temperature raised, coherency tends to break down and strength decreases. At the grain boundaries the ageing process is usually more advanced than that elsewhere and incoherent particles are precipitated. Grain boundary precipitates are illustrated in Fig. 1-6. The principal heat-treatable alloys are those based on Al-Cu (2000 series), Al-Mg-Si (6000 series), Al-Zn-Mg and Al-Zn-Mg-Cu (7000 series).

Although a fairly large number of casting alloys exist, most of them derive their properties from the addition of magnesium, silicon and copper either singly or in combination. The amount of magnesium can range from about 3 to 11%, that of silicon from 3 to 13% and that of copper from about 1 to 5%. They are produced in a range of tempers from 'as cast' to 'solution heat-treated' depending on alloy composition. Their basic structure is mainly that of dendritic cells in a matrix of aluminium. Some changes to the basic structure result from heat-treatment.