# **Materials – Microstructure and properties**

# Table of contents

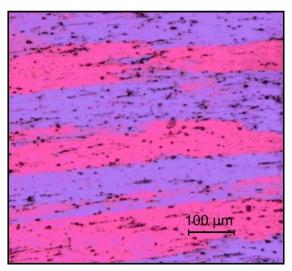
Microstructure and properties	2
4.1 Properties & microstructure determine the behaviour of automotive aluminium	2
4.2 Mechanical behaviour	
4.2.1 Mechanical behaviour: elastic behaviour, plastic behaviour and fracture behaviour	aviour3
4.2.2 Elastic behaviour	5
4.2.3 Plastic behaviour	7
4.2.4 Fracture behaviour	8
4.2.5 Effects of microstructure on ductility and fracture	10
4.2.6 Mechanical properties at elevated temperatures	11
4.2.7 Fatigue behaviour	
4.3 Physical properties	13
4.3.1 Physical properties of 99.99% pure aluminium	13
4.3.2 Physical properties of wrought alloys and casting alloys	14
4.4 Corrosion behaviour	15
4.4.1 Basic phenomena of corrosion of aluminium materials	
4.4.2 Protective oxide film	
4.4.3 Electrochemical nature of corrosion	
4.4.4 Influence of alloy composition	19
4.4.5 Pitting corrosion	
4.4.6 Intergranular corrosion	21
4.4.7 Stress corrosion cracking	
4.4.8 Exfoliation corrosion	23
4.4.9 Filiform corrosion	24
4.4.10 Galvanic corrosion	25
4.4.11 Crevice corrosion	28
4.4.12 Corrosion fatigue	29

# 4 Microstructure and properties

# 4.1 Properties & microstructure determine the behaviour of automotive aluminium

#### See also:

- △ AAM Materials 2 Alloy constitution
- AAM Materials 5 Wrought materials production > Automotive sheet
- △ AAM Materials 5 Wrought materials production > Extrusion
- ▲ AAM Products 6 Cast alloys and products



Microstructure of forged EN AW-6082-T6 etched acc. to Barker Source: ATS/ F. Ostermann

The usefulness of aluminium as engineering material is fundamentally related to the

- mechanical properties,
- ▲ physical properties and
- chemical properties

of the metal.

As a rule it is not a single individual property - like e.g. density - which determines its choice for a particular engineering application but a full spectrum of these properties.

## Example: heat exchangers

- ▲ density
- thermal conductivity
- ▲ corrosion resistance
- ▲ formability (ductility)
- strength at service temperatures.

On the other hand, **properties** of aluminium automotive materials and their behaviour during fabrication and service are intimately **related to alloy constitution** and **microstructure**.

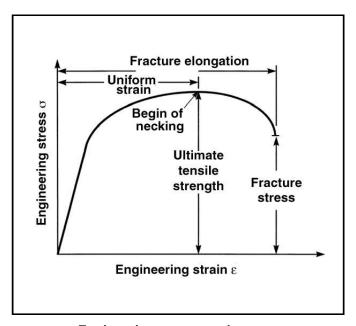
The purpose of this chapter is to describe the important engineering properties of **cast** and **wrought** aluminium materials and point out the effects of alloy and microstructural constitutions on properties and behaviour.

## 4.2 Mechanical behaviour

# 4.2.1 Mechanical behaviour: elastic behaviour, plastic behaviour and fracture behaviour

Link:

http://aluminium.matter.org.uk/aluselect/



**Engineering stress-strain curve** 

**Mechanical behaviour (strength, ductility, toughness) of aluminium** is described under the following aspects:

- A general characteristics,
- ▲ at room temperature,
- ▲ at low temperatures,
- ▲ at high temperatures,
- under tension and compression,
- under alternating (variable) loads,
- under impact loads (high loading rates),
- wrought, cast, welded microstructures.

The mechanical data of specific alloys: see relevant standards.

#### Definition of term "Aluminium" as engineering material:

- A aluminium alloys with varying degrees of alloy concentrations,
- A aluminium alloys with Rp0.2 ranging from 20 MPa to 600 MPa,
- wrought alloy materials in soft, strain-hardened and precipitation-hardened tempers,
- A casting alloys in as-cast, annealed, precipitation hardened tempers,
- consolidated powder metal and metal matrix compounds (MMC),
- anisotropy of ductility and strength caused by consolidation conditions (castings) and/or microstructure and texture (sheet, extrusions, forgings).

#### General characteristics of mechanical behaviour of "Aluminium":

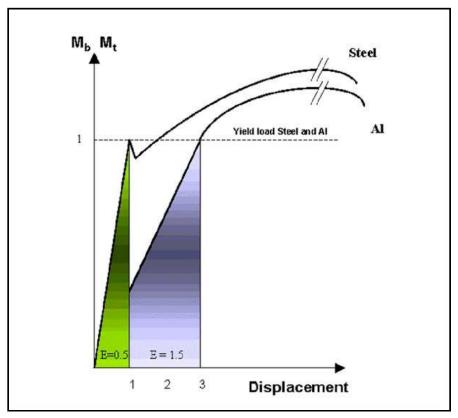
- aluminium's 12 independent slip systems (c.f. Fe: 48; Mg: 3!) provide ample basic ductility;
- high stacking fault energy -> easy cross-slip, wavy slip, no twinning;

- no ductile/brittle transition at low temperatures or high load rates;
   improved toughness at low temperatures and high load rates;
- little effect of low temperature or high load rates on Rp0.2;
  improved ductility above 100°C (0.4TM);
  decreasing creep resistance beyond 100°C.

## 4.2.2 Elastic behaviour

See also:

△ AAM – Design – 1 Design philosophy > Comparison to steel



Elastic energy absorption in aluminium and steel components

Source: Hydro Aluminium

## **Elastic behaviour**

Under tension or compression the slope of the initial part of the stress-strain curve determines the **Modulus of Elasticity** (Young's Modulus). Mostly, the rounded value of E = 70.000 MPa is used for aluminium and its alloys. It is 1/3 the value of steels.

Under torsion the Shear Modulus of **Modulus of Rigidity** is G = 26.000 MPa for aluminium compared to 82.700 MPa for steel.

**Poisson's Ratio** i.e. lateral strain divided by longitudinal strain is v = 0.33.

The modulus of elasticity (and rigidity) is only marginally dependent on alloy composition and temper, varying less than +/- 4% from the mean value of 70.000 MPa over the whole range of aluminium alloys.

The texture has a distinct influence. The modulus of elasticity is also varied by work hardening.

Contradictory information exists on the effect of microstructural conditions on the elastic constants. However, it is clear that the influence of a varying microstructure on the elastic properties of aluminium alloys is very small.

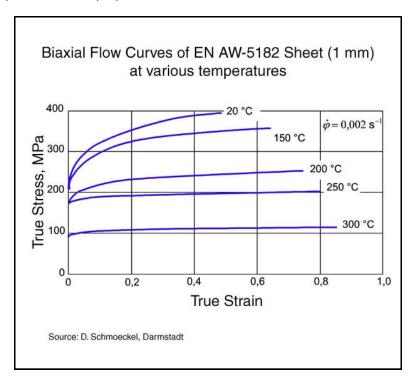
# Elastic energy absorption

Due to the lower E-modulus aluminium can absorb elastically the 3-fold amount of energy before plastic yielding compared with steel. This property is significant for crash-relevant components, like bumpers, etc.

#### 4.2.3 Plastic behaviour

See also:

▲ AAM – Products – 2 Extruded products > Tempers and mechanical properties > Tempers and static properties



## Yielding and plastic deformation

Aluminium and its alloys usually show a smooth transition from elastic to plastic deformation (designated by the value of Rp0.2). An exemption are the Al-Mg alloys with more than 2% Mg, which exhibit a **Luder's effect** in the annealed temper.

The onset of plastic yielding is generally not significantly strain-rate sensitive - in contrast e.g. to steels -, although there is a slight increase in yield strength at very high loading rates.

There is no difference between the yield stress in tension and compression.

Aluminium and all of its alloys **work-harden** over the whole temperature regime (also under cyclic straining), i.e. they show a **stable flow** characteristic.

The **rate of work-hardening** is not significantly strain-rate dependent until at temperatures above approx. 100°C.

Some alloys, particularly the Al-Mg alloys, show a **serrated flow curve**. The serrations appear after a few % of plastic strain, intensifying with increasing strain. This effect, called *Portevin-le-Chatelier* or dynamic strain ageing effect, may result in a growing surface roughness at larger strain levels. Above ambient temperatures the phenomenon disappears.

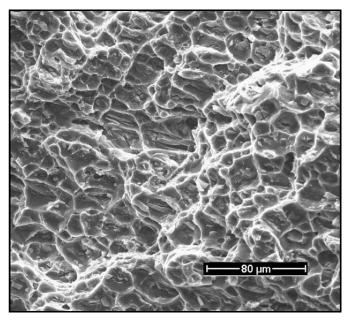
The **flow curve** can be described by the Ludwik-Holloman equation for parabolic flow. For detailed calculations various modification of the L-H equation have been proposed for better fit (see special chapters on flow curves for sheet and extrusion).

The flow curve is significantly influenced by **anisotropy** (texture) resulting from the thermomechanical history (examples for extruded and sheet alloys are given in other sections of the Manual.

#### 4.2.4 Fracture behaviour

#### See also:

- △ AAM Materials 2 Alloy constitution > Heat treatment > Annealing
- AAM Materials 2 Alloy constitution > Heat treatment > Solution treatment and ageing > Solution treatment
- AAM Materials 2 Alloy constitution > Heat treatment > Resolution treatment
- AAM Materials 2 Alloy constitution > Heat treatment > Retrogression heat treatment



REM photograph fracture of 6082-T6 forging Source: F. Ostermann, ATS

#### Typical ductile fracture mode

Fracture of aluminium and its alloys under static tensile loads at ambient and low temperatures occurs principally as "ductile fracture", i.e. by growth of microholes originating at microstructural discontinuities like precipitates or other constituent particles and by necking of the ligaments between holes, s. fig. above.

Fracture sites are regions of localised strain concentrations, as e.g. in the necking region of a tensile test bar.

Ductility is a materials property, but strongly dependent on the state of stress.

#### Effect of state of stress and strain

As with other ductile metals, plastic strain limits are strongly depending on the local state of stress and strain.

Therefore, measures of ductility have to be compared under comparable stress and strain conditions.

#### Common ductility measures:

- Fracture elongation [A5, A10, A80];
- ♣ Reduction in Area [Z];
- ▲ Forming limit diagram [FLD].

## Effects of strength level on ductility

As a general rule, the ductility of metals decreases with increasing strength level. In correspondence with this rule the ductility of aluminium alloys decreases

- with increased degree of work-hardening,with increased age-hardening,
- with increased alloy content.

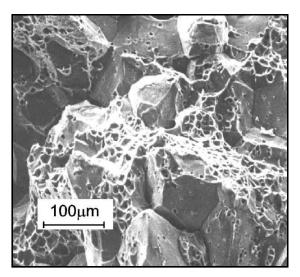
There are, however, several possibilities to obtain increased ductility levels by suitable heat treatments.

Furthermore, there are a number of microstructural influences on ductility, s. next page.

## 4.2.5 Effects of microstructure on ductility and fracture

#### Literature:

Altenpohl, D., Aluminium von innen, Düsseldorf: Aluminium-Verlag, 1994, ISBN 3-87017-235-5



REM photograph of mixed trans- & inter-granular fracture mode in AlSiMg alloy Source: B. Grcemba, VAW AG Bonn

#### Intergranular fracture

The normal fracture behaviour of aluminium and its alloys is independent of the magnitude of the elongation at fracture and characterised by a ductile, transcrystalline shear fracture mode. Brittle fracture without prior plastic deformation is an exception in aluminium alloys. It is based on <u>avoidable</u>, normally intergranular anomalies of the microstructure due to grain boundary precipitates or a tendency to stress corrosion. Transcrystalline, brittle cleavage fracture does not occur in aluminium.

A low ductility fracture can be caused by weakening of the grain boundaries due to particles which were formed preferentially at the grain boundaries. Such grain boundary precipitates can form e.g. in AlMgSi alloys with excess of Si, if these are cooled too slowly from solution heat treatment temperature. The fracture surface shows a mixture of brittle intergranular fracture and ductile shear fracture, s. fig. above.

## Impurity level

Ductility is also influenced by impurity elements, especially by the Fe-content. This is true for wrought as well as for casting alloys.

#### Other microstructural effects

Ductility will suffer from

- mixed microstructure (partial recrystallisation)
- A large dendrite arm spacing in castings,
- ▲ insufficient purification of melt (oxides),
- high hydrogen content in castings (pores),
- shrinkage porosity.

## 4.2.6 Mechanical properties at elevated temperatures

#### Literature:

- Ostermann, F., Anwendungstechnologie Aluminium, Berlin, Heidelberg, London, New York, Tokyo: Springer-Verlag, 1998, ISBN 3-540-62706-5
- Cobden R.: Aluminium: Physical Properties, Characteristics and Alloys. TALAT lecture 1501, EAA, 1994

The modulus of elasticity and the static strength values continuously decrease at elevated temperatures (see figure 1 and figure 2). One can assume a decrease in strength of approx. 5% at 100°C. A significant sharp decline of the elevated temperature strength values takes place at temperatures higher than 120°C. Under these conditions, creep processes may occur and creep becomes most important for temperatures above 200 – 250°C. For the strain-hardened and age-hardened alloys softening (recovery) or overageing, respectively, takes place in the same temperature range.

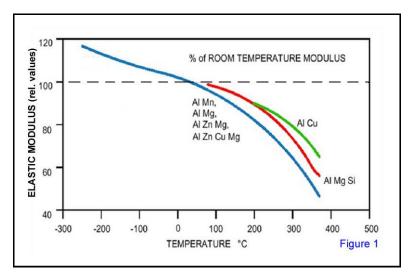


Figure 1: Modulus of Elasticity of Aluminium at various temperatures

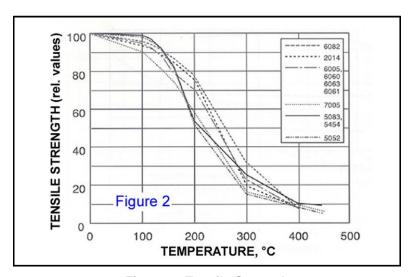


Figure 2: Tensile Strength

## 4.2.7 Fatigue behaviour

#### See also:

△ AAM – Design – 2 Performance > Fatigue

#### Literature:

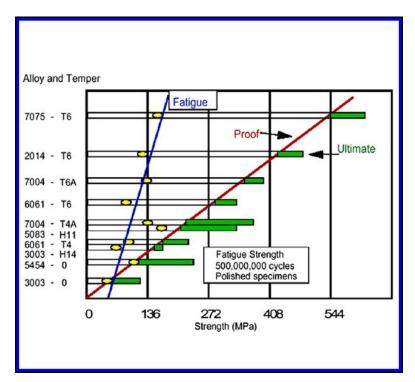
Cobden R.: Aluminium: Physical Properties, Characteristics and Alloys. TALAT lecture 1501, EAA, 1994

The fatigue (endurance), proof and ultimate tensile strengths of a number of Al alloys are compared in the figure at right. The fatigue strength was determined using rotating-beam tests at 5 x 10<sup>-8</sup> cycles using polished specimens.

In practice, the fatigue resistance is considerably reduced by local stress raisers such as sharp grooves, shoulders, abrupt changes in profile or even machining marks and scratches. This is particularly the case when the surface imperfection or stress raisers run across the direction of the stress field.

Such surface inhomogeneities produce small zones of intensified stress which have a far greater influence on the fatigue strength than the differences which can be attributed to the application of different alloys. Design and manufacture are therefore always the key elements in influencing the fatigue resistance of a component or structure.

These last statements are particularly true when considering welded structures and they hold true both for Al and steel.



Fatigue, proof and ultimate tensile strengths of some wrought aluminium alloys

# 4.3 Physical properties

## 4.3.1 Physical properties of 99.99% pure aluminium

A survey of important physical properties of 99.99% purity aluminium is given in the table below.

Physical property	Value	Unit
Atomic number	13	
Atomic weight	26.98154	
Crystal structure	Face-centered cubic	
Lattice parameter	0.40496	nm
Density	2.6989 x 10 <sup>3</sup>	kg/m³
Volume contraction liquid/solid	7.1	%
Linear contraction (660 - 20°C)	1.85	%
Coefficient of thermal expansion (20 - 100°C)	23.6 x 10-6	1/K
Modulus of elasticity	66.6	kN/mm <sup>2</sup>
Modulus of rigidity	25.0	kN/mm <sup>2</sup>
Poisson's ratio	0.35	
Melting temperature	660.2	°C
Heat of fusion	390	kJ/kg
Heat of evaporation	11.4	MJ/kg
Specific heat (at constant pressure)	0.89	kJ/kg K
Activation energy of self-diffusion	120	kJ/mol
Electrical conductivity	37.67	$m/\Omega$ mm <sup>2</sup>
Thermal conductivity	235	W/m K
Heat of combustion	31	MJ/kg
Magnetic susceptibility	0.62 x 10-9	m³/kg

Table of physical properties of 99.99% pure aluminium

Many of the properties shown in this table depend on temperature, degree of purity resp. chemical composition and pressure. For most of the cases in application technology the pressure dependence of physical properties practically does not play any role.

The physical properties of selected wrought and cast alloys are shown in the following screen.

# 4.3.2 Physical properties of wrought alloys and casting alloys

Alloy EN AW-		Density	Melting range	Electrical conductivity	Thermal conductivity	Specific heat	Coefficient of thermal expansion	Modulus o
Chemical symbols	Numerical	g/cm <sup>3</sup>	•c	m/Ω mm²	W/m K	J/kg K	10 <sup>-6</sup> /K	N/mm²
Al99.5	1050A	2.70	645 - 658	34.5	229	899	23.5	69'000
Al99.0	1200	2.72	645 - 657	33.9	225	898	23.4	69'000
AlMn1Cu	3003	2.73	640 - 655	24.4 - 29.4	190	892	23.1	69'500
AlMn1	3103	2.73	640 - 655	24.4 - 29.4	190	892	23.1	69'500
AlMn1 Mg1	3004	2.72	629 - 654	23 - 25	160 - 190		23.2	
AIMg1 (B)	5005	2.70	630 - 655	30.3	201	897	23.5	69'500
AIMg2	5251	2.69	605 - 650	21.7	149	898	23.6	70'000
AIMg2.5	5052	2.68	605 - 650	20.2	138	901	23.7	70'000
AIMg3	5754	2.68	595 - 645	18.9	132	897	23.7	70'500
AIMg3Mn	5454	2.69	600 - 645	19.6	135	897	23.6	70'500
AIMg4.5Mn0.4	5182	2.65	575 - 640	18.0	123	904	24.1	71'000
AIMg4.5Mn0.7	5083	2.66	580 - 640	16.7	117	899	23.8	71'000
AIMgSi	6060	2.70	610 - 655	28.6 - 31.3	187 - 209	898	23.4	69'500
AlMg1 SiCu	6061	2.70	580 - 650	23.2 - 27.0	155 - 180	895	23.3	70'000
AIMg0.7Si	6063	2.70	615 - 655	28.6 - 32.2	193 - 218	898	23.5	69'500
AlSiMg(A)	6005A	2.71	605 - 655	28.6	193	892	23.3	69'500
n renerous <del>e</del> ncovies	(6016)1	2.70	585 - 650	26 - 30	160 - 190	894	23.4	69'500
	(6022)1	2.69	580 - 650				23.4	
	(6111)1	2.71	585 - 650	23			23.4	
	(6181A)1	2.70	585 - 650	26 - 30	160 - 190	894	23.4	70'000
AISi1 MgMn	6082	2.71	575 - 650	24.4 - 32.3	172 - 216	894	23.1	70'000
AlCu4MgSi(A)	2017A	2.79	510 - 645	19.6	134	873	22.9	72'500
AlCu4Mg1	2024	2.79	500 - 640	17.5 - 29.4	121 - 193	874	23.1	73'000
AlCu4SiMn	2014	2.80	505 - 640	19.6 - 29.4	134 - 192	869	22.7	73'000
AlZn4.5Mg1	7020	2.78	605 - 645	20.4	139 - 140	873	23.3	70'000
AlZn5.5MgCu	7075	2.81	475 - 635	19.2 - 26.3	134 - 175	862	23.5	72'000

Selected physical properties of wrought aluminium alloys
Source: EAA/ALUSELECT

Alloy EN AC-	Density	Melting range	Electrical conductivity	Thermal conductivity	Coefficient of thermal expansion	Modulus of rigidity
	g/cm <sup>3</sup>	°C	m/Ω mm²	W/m K	10 <sup>-8</sup> /K	N/mm²
AlSi12(Cu)	2.65	530 - 580	16 - 23	110 - 160	20	75'000
AlSi10Mg(Cu)	2.65	530 - 600	16 - 20	110 - 140	20	74'000
AlSi9Cu3	2.75	490 - 600	14 - 18	100 - 130	22	75'000
AISI11	2.65	570 - 590	18 - 27	130 - 190	21	75'000
AlSi7Mg3	2.70	550 - 610	22 - 24	160 - 170	22	73'000
AlSi10Mg	2.65	550 - 600	17 - 26	120 - 180	20	75'000

Selected physical properties of some casting alloys Source: EAA/ALUSELECT

## 4.4 Corrosion behaviour

## 4.4.1 Basic phenomena of corrosion of aluminium materials

#### See also:

- △ AAM Products 2 Extruded products > Corrosion resistance
- △ AAM Products 3 Automotive tubes > Corrosion properties
- AAM Products 3 Automotive tubes > Corrosion properties > Long Life Alloys (LLA)
- ▲ AAM Design 2 Performance > Corrosion > Galvanic corrosion Design guidelines for dissimilar joints

#### **Objectives**

This chapter is devoted to a description of the basic phenomena of corrosion of aluminium materials, as they may occur in automotive applications.

More specific details on the corrosion rating of alloys and on design and fabrication related aspects, especially those which may be experienced with dissimilar metal designs, are treated elsewhere in the Manual.

## General definition of corrosion (according to DIN 50900)

Corrosion is the reaction of a metal with its environment that leads to a measurable change of the material and can impair the function of a part or of a system.

The generally good corrosion resistance of "aluminium" is based on the stability and adherence of its natural, protective oxide film. Since the bare metal is rather reactive in aqueous environments, corrosion attack is only experienced where the protective oxide film is penetrated or destroyed and prevented from regeneration.

## 4.4.2 Protective oxide film

Literature:

A Pourbaix, M.: Atlas of electrochemical equilibria in aqueous solutions, Pergamon Press, 1966, p.171

The natural compact and adherent film of aluminium oxide forms when a fresh aluminium surface is exposed to air. On freshly rolled sheet the thickness of the oxide film is  $\sim$ 2.5 nm and grows over the years to  $\sim$ 10 – 20 nm.

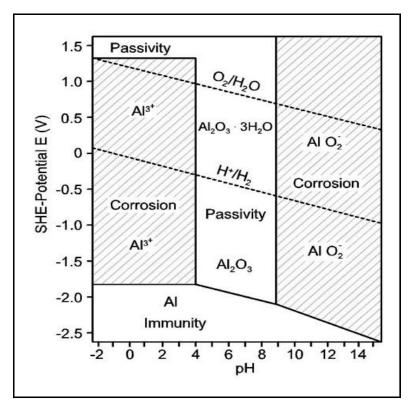
The Al-oxide film is stable over the range of pH  $\sim$ 4.5 to  $\sim$ 8.5. When the oxide film dissolves, e.g. in strong acids and alkalis, dissolution of the metal occurs too, i.e. the metal corrodes. Therefore aluminium is termed an amphoteric metal. The presence of certain anions (e.g. Cl $^{-}$ ) or cations (e.g. Cu $^{2+}$ ) also has an influence on the stability of the oxide film.

<u>Figure</u>: Pourbaix diagram for aluminium with an Al<sub>2</sub>O<sub>3</sub> x 3H<sub>2</sub>O film at 25°C. Potential values are for the standard hydrogen electrode (SHE).



Oxide layer with increased thickness ( $\sim$ 400 nm) produced by anodisation (H3PO4); M = 50.000x

The diagram shows the regions of immunity and passivity as a function of pH-value and electrode potential.



Potential-pH diagram according to Pourbaix for aluminium with oxide film in aequeous solution at 25  $^{\circ}$  C

## 4.4.3 Electrochemical nature of corrosion

#### Literature:

- Ostermann, F. and 8 Co-authors, Aluminium Materials Technology for automobile construction, English translation edited by Roy Woodward, London Mechanical Engineering Publications Limited, 1993, ISBN 0 85298 880 X
- Ostermann, F., Anwendungstechnologie Aluminium, Berlin, Heidelberg, London, New York, Tokyo: Springer-Verlag, 1998, ISBN 3-540-62706-5
- △ Ostermann, F. und 8 Mitautoren, Aluminiumwerkstofftechnik für den Automobilbau, Ehningen: Expert-Verlag, 1992, ISBN 3-8169-0773-3

**Corrosion is an electrochemical process**, i.e. it relies on electron transfer. Corrosion of aluminium can be split into an anodic and cathodic part- reaction which can occur at separate places on the metal surface provided that they are in electrical contact.

The **anodic reaction** is an oxidation process and releases electrons:

 $2 \text{ Al} \rightarrow 2 \text{ Al}^{3+} + 6 \text{ e}$  (in acid solutions)

Al + 4 OH $^{-}$   $\rightarrow$  Al(OH) $_{4}^{-}$  + 3 e (in neutral and alkaline solutions)

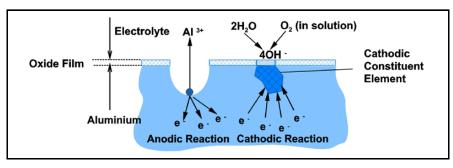
The **cathode reaction** is a reduction process and accepts electrons:

 $6 \text{ H}^+ + 6 \text{ e}^- \rightarrow 3 \text{ H}_2$  (in acid solutions)

 $3 \text{ H}_2\text{O} + 3 \text{ e}^- \rightarrow 3 \text{ OH}^- + 3/2 \text{ H}_2$  (in alkaline solutions)

O<sub>2</sub> + 2 H<sub>2</sub>O + 4 e<sup>-</sup>  $\rightarrow$  4 OH (in aerated solutions)

The rate of electron transfer between the anodic and cathodic reactions is a measure of the corrosion rate (often called corrosion current).



Schematic of the electrochemical corrosion mechanism of Al Source: F. Ostermann, Lit.

## 4.4.4 Influence of alloy composition

#### Literature:

▲ Textor M., Néma P., Timm J.: Car body alloys and methods of corrosion protection: aluminium sheet; Mat.-wiss. u. Werkstofftech. 26 (1995) 318 - 326

The type, extent and progress of corrosive attack are influenced both by the environmental conditions including part design and by the chemical composition, the microstructure and the surface characteristics of the material.

The higher the purity of aluminium, the greater is its corrosion resistance.

Alloying elements that are added to achieve certain material properties, e.g. to increase the material strength, change the electrochemical behaviour of pure aluminium. Important factors are the type and concentration of the added elements, e.g. whether they are present in solid solution or as intermetallic particles.

In the table below the corrosion potentials are given of some intermetallic phases and their electrochemical behaviour relative to the aluminium matrix.

The grain structure, the type and size of intermetallic particles and their distribution, e.g. preferential precipitation along grain boundaries or homogeneous distribution, are influenced by the processing conditions. This allows controlling the microstructure with respect to corrosion resistance.

Alloying element	Intermetallic phase	Potential (V)	Behaviour relativ	
N4	Mar Al (a Mar Al )	4.04		
Mg	$Mg_5Al_8$ ( $\beta$ - $Mg_2Al_3$ )	-1.24	anodic	
Mg + Zn	MgZn <sub>2</sub>	-1.05	anodic	
Mn	MnAl <sub>6</sub>	-0.85	~neutral	
Mg + Si	Mg <sub>2</sub> Si	-0.83	~neutral	
Cu	CuAl <sub>2</sub>	-0.73	cathodic	
Fe	FeAl <sub>3</sub>	-0.56	cathodic	
Ni	NiAl <sub>3</sub>	-0.52	cathodic	
Si	Si	-0.26	cathodic	
-	AI 99.95	-0.85	-	

Reference: 0.1 n calomel electrode

## Corrosion potentials of intermetallic phases measured in 1 n NaCl + 8g/l H2O2

The table below shows a rough listing of aluminium alloys regarding their corrosion resistance.

Wrought alloys	Cast Alloys
High purity aluminium Pure aluminium AIMn AIMg AIMgMn AIMgSi AIZn / AIZnMg AIZnMgCu AICu	Pure aluminium  AlMg(Si)  AlSiMg  AlSi(Cu)  AlZnMg  AlCuMg  AlCu
AlCuMg	AlCuMg

Rough listing of Al alloys regarding their corrosion resistance

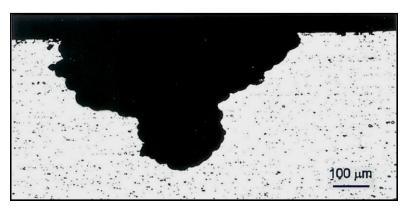
## 4.4.5 Pitting corrosion

#### Literature:

Textor M., Néma P., Timm J.: Car body alloys and methods of corrosion protection: aluminium sheet; Mat.-wiss. u. Werkstofftech. 26 (1995) 318 - 326

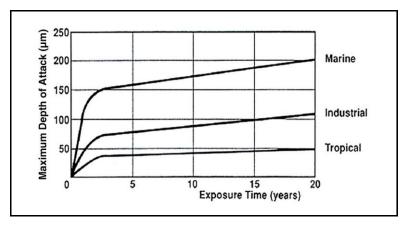
**Pitting corrosion** occurs when small localised "anodic" areas are present on an otherwise passive surface (see Pourbaix diagram, page 2) in an aggressive aqueous solution, e.g. containing chloride or heavy metals. The negative effect of chloride ions can be explained by penetration of the ions through the oxide layer.

Pitting corrosion leads to more or less circular pits of variable size. The amount of metal loss is relatively small and static strength properties of the material are nearly not affected.



Typical appearance of pitting corrosion: local attack with irregular distributed, virtually roundish dimples of variable size

In contact with neutral, weak acidic or alkaline solutions the metal loss is only small, s. figure below. Furthermore often undissolvable corrosion products are formed that hinder further corrosive attack.



Maximum depth of local corrosive attack of aluminium alloys in different climates (typical evolution,  $d \sim t^{(1/2)}$ )

## 4.4.6 Intergranular corrosion

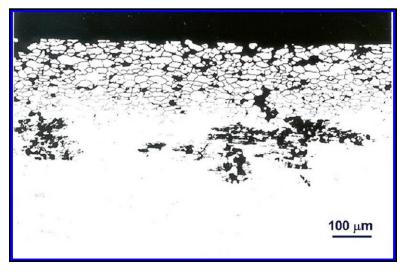
#### Literature:

- ▲ Textor M., Néma P., Timm J.: Car body alloys and methods of corrosion protection: aluminium sheet; Mat.-wiss. u. Werkstofftech. 26 (1995) 318 326
- △ Godard, P., Aluminium. In The corrosion of light metals, New York-London-Sidney: John Wiley & Sons, Inc., 1967
- Metals HandBook. Volume 13, Corrosion, ASM International, 1987
- △ Vargel C., Corrosion de l'aluminium, Dunod, Paris, 1999ISBN 2 10 0041916

**Intergranular corrosion (IC)** is a form of localised subsurface attack in which a narrow path is corroded out preferentially along the grain boundaries of the metal. The corrosion mechanism is electrochemical and depends on the presence of local electrolytic cells at the grain boundaries. The local cells are usually caused by the presence of intermetallic particles at the grain boundaries and adjacent denuded zones having a different solution potential. The precipitates may be anodic, e.g. as MgZn2 or AlsMg5, and corrode preferentially. Or they may be cathodic, e.g. as CuAl2, in which case they do not corrode but stimulate corrosion of the adjacent denuded zone. In either case selective grain boundary corrosion occurs.

The degree of susceptibility of an alloy to intergranular corrosion can thus vary appreciably, depending on its microstructure (amount, size, distribution of second phase particles) which is the result of its metallurgical history and thermal treatment. Heat treatments that cause precipitation throughout the grain tend to diminish the sensitivity to intergranular corrosion.

Intergranular corrosion can lead to a loss of mechanical properties depending on the depth of penetration into the metal.



Typical appearance of intergranular corrosion: preferred local dissolution of metal under the surface along the grain boundaries

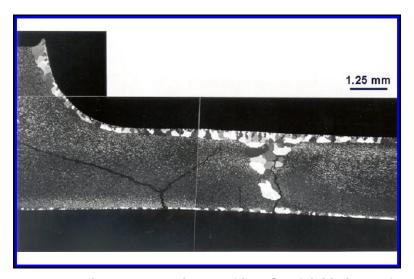
IC can occur in alloys in which grain boundary precipitates exist which have a different solution potential as the aluminium matrix, e.g. AlCu alloys. For more information see Lit.

## 4.4.7 Stress corrosion cracking

Stress corrosion cracking (SCC) is characterised by a propagation of intergranular cracking due to the presence of stress intensities well below the fracture toughness in an elastically loaded material. SCC requires a combination of:

- A a corrosive environment, e.g. a chloride containing electrolyte
- A residual internal or applied tensile stress beyond a threshold limit
- A susceptible microstructure of the material allowing an easy crack propagation.

SCC is characterised by a brittle failure in a material that is otherwise ductile. The crack propagates in a plane perpendicular to the direction of applied stress. In the absence of either a continuous tensile stress or a corrosive environment, cracking does not occur. The mechanism of stress corrosion failure of aluminium alloys involves both electrochemical and mechanical processes. In the first stage intergranular corrosion attack occurs by local corrosion cell action. In the corroded area small cracks develop by mechanical stresses. This leads to further electrochemical action and to a deepening of the cracks. SCC can occur in AlCu-, AlMg-, AlZnMg(Cu)-, and AlLi-alloys when a susceptible microstructure is present and the pre-conditions mentioned above are fulfilled.



Typical appearance of stress corrosion cracking: Crack initiation at the surface, preferentially at coarse grain zones, crack propagation intergranular; AlZn4.5Mg1 extrusion, anodised in Barker's reagent

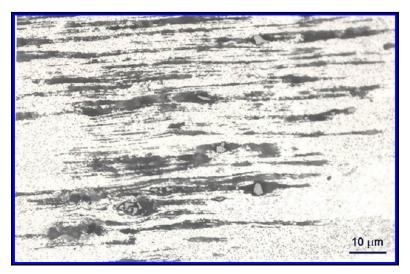
## 4.4.8 Exfoliation corrosion

#### Literature:

△ Ostermann, F., Anwendungstechnologie Aluminium, Berlin, Heidelberg, London, New York, Tokyo: Springer-Verlag, 1998, ISBN 3-540-62706-5 — s. chapter 5.4, page 124, especially fig. 5.4.8

**Exfoliation corrosion**, also called layer or lamellar corrosion, is a specific type of selective attack that proceeds along multiple narrow paths given by the microstructure of the material parallel to the surface of the metal. Generation of corrosion products forces the layer apart and causes the metal to swell. Flakes of metal may be pushed up and even peel from the surface. The usual preferential corrosion paths are along grain boundaries, if these are in the same direction due to mechanical working, e.g. in extrusions with fibrous grain structure or in sheet with high degree of cold rolling.

Exfoliation corrosion can occur in AlCu-, AlMg-, AlZnMg(Cu)-alloys when the material is in a sensitive temper. In AlZnMg alloys the heat affected zones of fusion welds are sensitive to exfoliation corrosion, unless the component is subjected to an additional re-aging at 120°C, s. Lit.



Typical appearance of exfoliation corrosion: lamellar corrosion attack parallel to the metal surface preferably along the grain boundaries. Corrosion products press individual, not attacked layers apart → lamellar delaminations. AlZnMg extrusion alloy: primary Al(Fe,Mn)Si precipitates act as cathodic attack of the Al matrix.

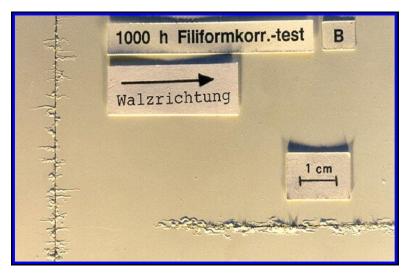
## 4.4.9 Filiform corrosion

#### Literature:

- △ Bleeker, R., Bottema, J., Sibson, J., Gehmecker, H., Johannpötter, O.: Filiform Corrosion of Painted Al Body Sheet AA6016 with Special Attention to Alloying Element Copper. Proc. ASST2000, (2000)
- Bleeker, R., Lahaye, C.T.W.: Filiform corrosion of painted aluminium automotive body sheet with special attention to the alloying element copper. Proc. of Eurocorr2000 (2000)

**Filiform corrosion** appears as worm like tracks tunnelling under a surface coating, e.g. an anodisation or lacquer layer on the aluminium surface. The attack takes place at the metal/coating interface.

This type of corrosion can occur when the surface coating has insufficient barrier properties or is damaged and the aluminium surface has not been pretreated accordingly, e.g. by means of pickling or a conversion pre-treatment. Further important influencing factors are the relative humidity and the presence of corrosive agents, e.g. chlorides.



Typical appearance of filiform corrosion: vermicular attack of surface-coated, e.g. painted or anodised aluminium components at the interface metal/coating.

#### 4.4.10 Galvanic corrosion

#### See also:

△ AAM – Design – 2 Performance > Corrosion

#### Litterature:

Metals Handbook, volume 13 Corrosion, ASM Ohio 1987

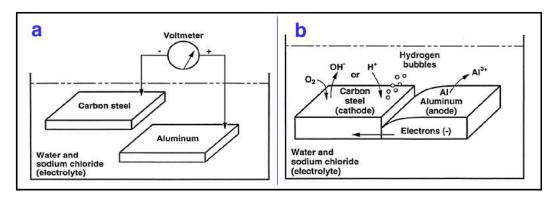
#### Galvanic cells

An electrical potential, or voltage, difference exists between two dissimilar metals when they are immersed in a conductive solution, or *electrolyte*. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron (current) flow between them.

The metal from which the electrons flow is termed the *anodic*, or *less noble*, metal; the metal to which the electrons flow is termed the *cathodic*, or *more noble*, metal. As the electron flow proceeds, the **anodic metal dissolves** (or oxidizes) in the conductive solution. The dissolution process is termed *galvanic\* corrosion* and the combination of the two metals in the conductive solution is called a *galvanic\* cell* or *galvanic\* couple*.

The dissolution (corrosion) rate of the anodic metal is proportional to the magnitude of the electric current, or corrosion current between the two metals.

Figure below: typical galvanic couple. The anodic metal is aluminum and the cathodic metal is carbon steel. If the metals are not touching each other (left figure) a voltage difference can be measured between the two metals; however, the corrosion rates of each metal remain independent of the other because no path exists for electrons to travel between them. If the metals are connected to each other (right figure), electrons can travel from the anodic metal, aluminum, to the cathodic metal, carbon steel.



#### **Corrosion potentials**

The voltage of each individual metal, and hence the voltage difference between any two metals, can be measured. Voltages of individual metals are called the **electrode potential** or **corrosion potential** of that metal. They are usually measured with respect to some reference electrode (usually saturated calomel reference electrode (SCE) in a sodium chloride solution). The difference in corrosion potential of two coupled materials provides a rough first approximation of the relative galvanic corrosion rate (see Table below). As a simple approximation, the greater the potential difference between two coupled metals, the greater the possibility that galvanic corrosion will occur. It must be stressed, however, that this is only a simplistic, rough approximation.

	Metal	Electrode Potential [Volts vs. Saturated Calomel Electrode]
	Chromium	+0.05 to +0.27
	Nickel	+0.12
More	Stainless Steel	0.0
Cathodic	Copper	-0.11
	Mild Steel	-0.50 to -0.55
	Lead	-0.71
More Anodic	2XXX aluminum alloys	-0.71 to -0.55
	6XXX aluminum alloys	-0.73 to -0.70
	5XXX aluminum alloys	-0.78 to -0.76
	7XXX aluminum alloys	-0.87 to -0.75
	Zinc	-1.01
<b>'</b>	Magnesium	-1.64

1 Measured in a solution of 53 g/liter NaCl + 3 g/liter H2O2 per ASTM G69
2 Potentials are versus Saturated Calomel Electrode (SCE). The potentials in the Metals HandBook are versus 0.1N Calomel. (mVSCE = mV0.1N + 92mV)

#### Corrosion potentials for a variety of metals and alloys

#### Polarization - change of potential

The corrosion potential of a metal is measured under conditions of **no current flow**. As a current is passed to or from a metal, its potential changes. The change is called polarization. When two metals are coupled, the galvanic current that flows between them causes them to be polarized to the same potential. In some cases, the potential of the anodic metal changes, or becomes polarized, to a value close to the potential of the cathodic metal. In other cases, the potential of the cathodic metal changes, or polarizes, to a value close to that of the anodic metal. In the former case rapid corrosion of the anodic metal takes place; in the latter, little corrosion of the anodic metal occurs.

Thus, the extent of galvanic corrosion which occurs is not only dependent on the initial potential difference and environment (as discussed above), but the extent to which each member of the galvanic couple is polarized.

For example, the potential difference between **aluminium** and **stainless steel** is greater than the potential difference between aluminium and copper measured in a neutral chloride solution (see Table 1). Yet, stainless steel is galvanically compatible with aluminium, but copper is not. This is because stainless steel is easily polarized toward the potential of aluminium, while copper is not. Therefore, aluminium corrodes more readily when in contact with copper than when in contact with stainless steel.

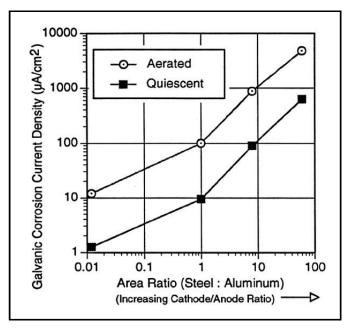
The same is true for aluminium coupled to mild steel vs. aluminium coupled to stainless steel. While the potential difference for aluminium/mild steel is smaller than that for aluminium/stainless steel, the galvanic corrosion rate for aluminium coupled to mild steel is far greater than that for aluminium coupled to stainless steel. This is again because stainless steel is easily polarized toward the potential of aluminium, while mild steel is not.

#### Anode to cathode area ratio

In addition to the potential difference and polarization of the cathodic metal, the magnitude of the corrosion depends on the **relative areas of the dissimilar metals**. The cathodic member of the couple often dominates the corrosion reaction rate. Therefore, an increase in cathodic area results in a higher rate of corrosion at the anode.

Thus, galvanic corrosion can be minimized by reducing the cathodic area and/or increasing the anodic surface area.

The figure below illustrates this effect for alloy 6111 (Al-Mg-Si-Cu), coupled to bare (not galvanized) mild steel (test environment: 3.5 weight % NaCl).



Galvanic couple: Alloy 6111 / Mild Steel (not galvanised)

Test environment: 3.5 weight % NaCl

This data is from a laboratory electrochemical experiment. The two specimens are coupled through a zero-resistance ampere meter, which allows the galvanic current to be measured without external influence from the measuring electronics.

Increasing galvanic current density indicates an increased rate of galvanic corrosion for the aluminium.

#### **Environment**

The **electrical conductivity** of the solution or electrolyte is an important factor in corrosion. For example, more corrosion will occur on aluminium coupled to steel in high conductivity sodium chloride solution (e.g., road salt splash) than will occur in plain water. A more practical illustration is the difference in corrosion occurring in the splash zone of an automobile (fenders, door, etc.) exposed to a chloride containing de-icing salt as opposed to the corrosion that occurs above the splash zone (hoods, deck lids, etc.).

The **oxygen content** of the electrolyte is also a critical factor. Consider as an example a typical 6XXX series aluminium alloy coupled to mild steel (cathode). The severity of galvanic corrosion is to a large extent governed by the rate of reaction at the cathode. The cathodic reaction rate on steel is highly dependent upon the concentration of oxygen in solution. When exposed to the same solution, but now actively aerated (i.e., air bubbled into it) the corrosion currents increase by roughly an order of magnitude.

This is illustrated for alloy 6111 on the previous screen. Note that due to the additional oxygen available for cathodic activity the difference between aerated and quiescent is roughly an order of magnitude.

This example is given to further illustrate the need for **caution when using electrode potentials** as a guideline for galvanic corrosion performance, without considering other factors. The environment that the potentials were measured in is a highly oxygenated environment. Many application environments are not actively aerated or oxygenated. Using electrode potentials as a guideline may provide unrealistically severe estimations of danger of galvanic corrosion.

#### 4.4.11 Crevice corrosion

Between adjacent aluminium surfaces in close contact, forming a crevice, localised corrosion can occur on entry of humidity.

The critical crevice width is ~0.02 to 0.5 mm.

This type of corrosion, termed crevice corrosion, is enhanced by additional presence of dirt or salt, e.g. in marine environment or by winter de-icing salts.

The cause of crevice corrosion is the formation of a local galvanic cell consisting of the inside of the crevice exhibiting a depletion of the oxygen content of the electrolyte and the oxygen rich outside surface (cathode).

A further influencing factor is the formation of acidity within the crevice causing a pH decrease. Crevice corrosion is especially pronounced when the crevice is formed by metals with different electrochemical behaviour (s. galvanic corrosion). If the crevice or the cathode surface dries out, corrosion stops.

Generally the amount of aluminium consumed by crevice corrosion is small. It is, however, of practical importance for metal with thin cross section, e.g. foil, and in cases in which surface appearance is important. Furthermore the production of bulky corrosion products in a confined space can exert a strong disruptive force and lead to the distortion of assemblies made from heavy sections.

## 4.4.12 Corrosion fatigue

The fatigue life of aluminium components decreases substantially when simultaneous loading by fatigue and corrosion occurs.

The resulting reduction in the fatigue life depends on the material (alloy composition and microstructure) as well as on the geometry of the component. The stress concentration factor plays a major role in this respect. Whereas for small notches, the fatigue life is reduced by a factor of 2-3 by the presence of a corrosive environment, the reduction factor may reach up to 5-6 for deep notches.

Corrosion fatigue is most relevant for alloys and microstructures which are corrosion-sensitive per se. It can be seen clearly that the fatigue performance of AA 5182 alloy is significantly influenced by salt spray corrosion. This effect is most pronounced in the high cycle region.

