TALAT Lecture 5102

Reactivity of the Aluminium Surface in Aqueous Solutions

13 pages, 10 figures (also available as overheads)

Basic Level

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Objectives:

- better understanding of the electrochemistry of Aluminium
- introduction to the other lectures

Prerequisites:

- knowledge of aluminium metallurgy
- knowledge of simple chemistry (thermodynamics and kinetics)
- knowledge of electricity
- basic knowledge of general electrochemistry

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5102 Reactivity of the Aluminium Surface in Aqueous Solutions

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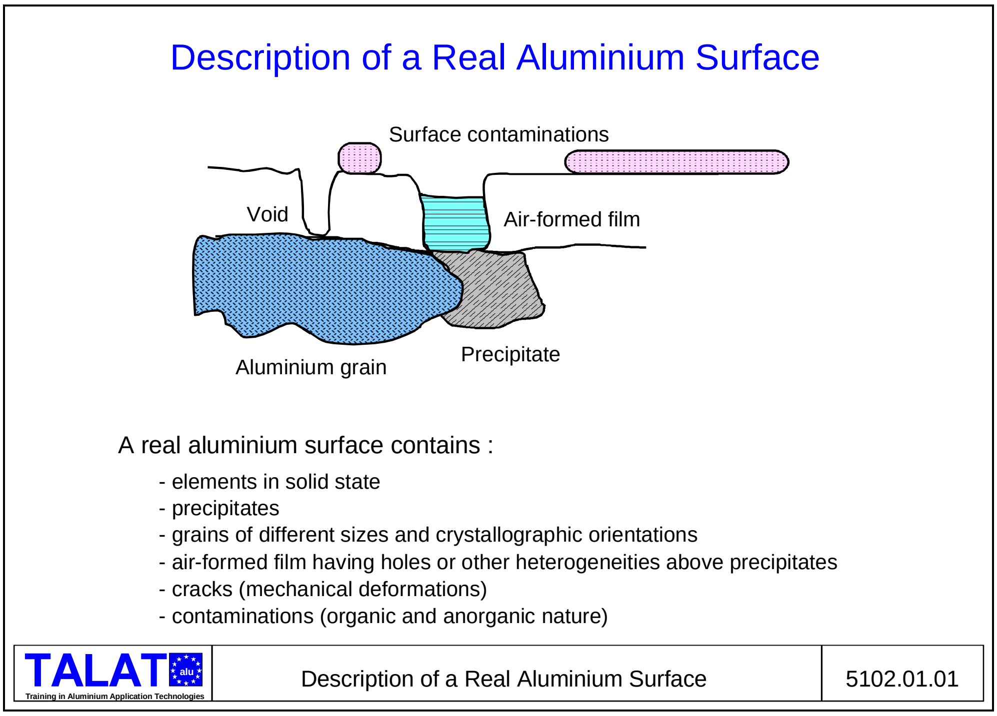
5102.01 Introduction

This lecture deals with the understanding of the reactivity of an aluminium surface in different aqueous solutions. It is obvious that the knowledge of the reactivity of aluminium surfaces in aqueous solutions is the key factor in mastering surface treatment processes and in preventing corrosion.

Considering the reactivity of the aluminium substrate the electrochemistry of aluminium becomes important. So this lecture will basically deal with the electrochemical behaviour of aluminium in water solutions. The aim is to repeat some basic principles of electrochemistry and to use them for aluminium.

In **TALAT Lecture 5101** a description of the "real" aluminium surface was given taking into account the presence of the alloying elements, the presence of the oxide layer, the presence of contamination, etc. A schematic representation of such a surface is given in **Figure 5102.01.01**. In the first part of this lecture this complicated view will be simplified to introduce the basic concepts of electrochemistry and its use for aluminium. Afterwards they will be applied on the true aluminium surface to explain the anodic and cathodic polarization behaviour of aluminium in different water solutions. Links will be discussed to surface treatment processes and corrosion effects.



Description of a Real Aluminium Surface

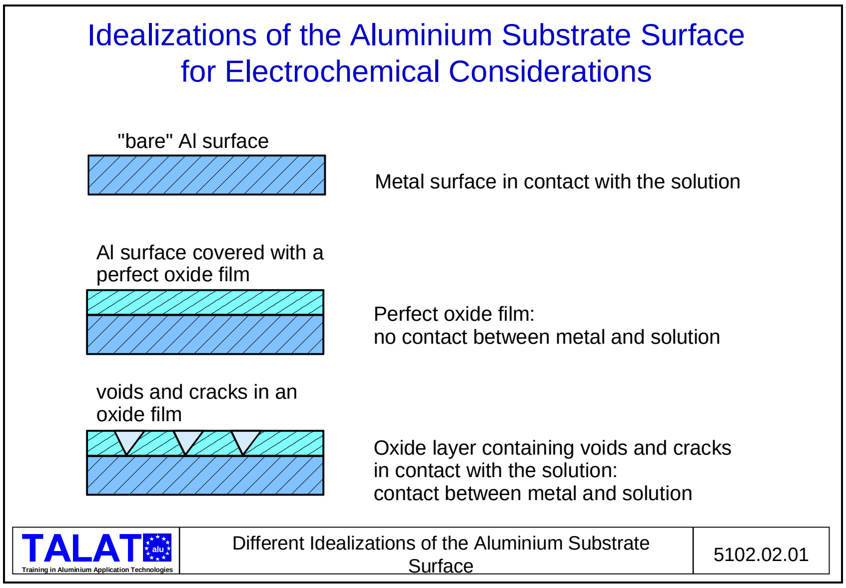
A real aluminium surface contains :

- elements in solid state
- precipitates
- grains of different sizes and crystallographic orientations
- air-formed film having holes or other heterogeneities above precipitates
- cracks (mechanical deformations)
- contaminations (organic and anorganic nature)

TALAT Training in Aluminium Application Technologies | Description of a Real Aluminium Surface | 5102.01.01

5102.02 Basic Electrochemical Principles

Before we start to introduce the electrochemical basic principles it is important to simplify the aluminium substrate which was introduced in **Figure 5102.01.01**. **Figure 5102.02.01** shows three possible images which can be used. In the first case we ignore the presence of any oxide layer and consider the aluminium as a bare homogeneous surface in contact with the solution. The classical electrochemistry theory - where we are dealing with a perfect metal/solution interface which can be polarized - is than applicable. We will use this image to introduce the basic electrochemical concepts on the aluminium surface. A second possible image is the one where the aluminium substrate is completely covered with an isolating oxide layer. As the aluminium oxide layer is electrically isolated, its electrochemistry is rather simple because there is none, the substrate is electrochemically immune. The third image is already closer to the image given in **Figure 5102.01.01** where we consider to have an aluminium substrate covered with an oxide layer where parts for one or another reason are imperfect and where contact between metal and solution becomes possible. That image will be used at the end of this lecture to explain some polarization differences in different aqueous solutions.



Idealizations of the Aluminium Substrate Surface
for Electrochemical Considerations

"bare" Al surface

Metal surface in contact with the solution

Al surface covered with a perfect oxide film

Perfect oxide film:
no contact between metal and solution

voids and cracks in an oxide film

Oxide layer containing voids and cracks
in contact with the solution:
contact between metal and solution

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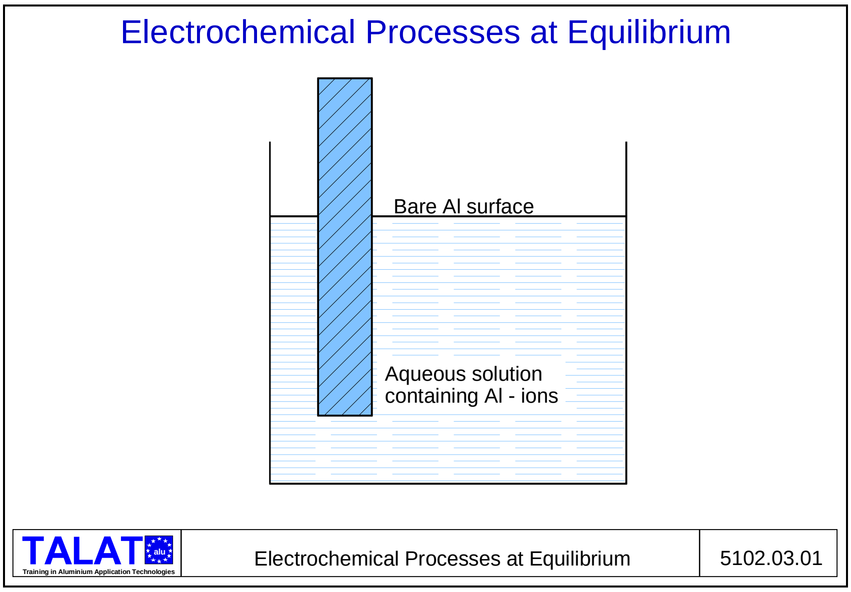
Different Idealizations of the Aluminium Substrate Surface

5102.02.01

5102.03 The Aluminium Surface under Equilibrium Conditions

The introduction of some important electrochemical concepts will be done in two parts. First, we will discuss the situation of the aluminium surface under thermodynamic equilibrium, meaning, we will discuss the possible reactions and their thermodynamic properties. Next, the behaviour of aluminium will be discussed under driven processes (non-equilibrium conditions).

Consider first the situation where an aluminium surface is dipped into an aqueous solution containing only Al^{3+} ions (**Figure 5102.03.01**).



Electrochemical Processes at Equilibrium

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Electrochemical Processes at Equilibrium

5102.03.01

The potential between electrode and solution can be calculated from the Nernst equation:

$$E_{o\,Me/Me^{z+}/NHE} = E^{o}_{o\,Me/Me^{z+}/NHE} + RT/zF \ln a_{Me^{z+}}$$

where
E_o = the equilibrium potential or Nernst potential (in mV)
E_o^o = the standard equilibrium or Nernst potential (in mV)
a_{Mez+} = the activity of the metal ions (a_{Me} is considered to be 1)
z = number of electrons
F = Faradaic constant
NHE = Normal Hydrogen Electrode

In the case of an aluminium surface in contact with a solution containing Al ions the following reaction must be considered:

$$Al \Leftrightarrow Al^{3+} + 3e^-$$

The Nernst equation becomes

$$E = E_o^o + RT/zF \ln a_{Al}{}^{3+}$$

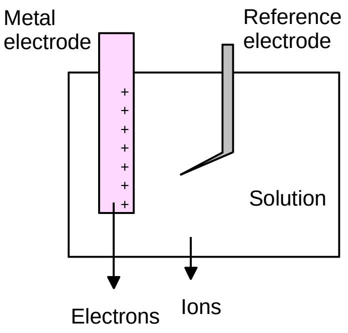
$$E = E_o^o + 0.059\ RT/3F \log [Al^{3+}]$$

where

E_o is the Nernst potential
E_o^o is the standard Nernst potential.

To measure this equilibrium potential we must be able to measure the electrode potential. The electrode potential is the potential which exists between electrode and solution. Unfortunately, the absolute potential difference between electrode and solution cannot be measured directly as a potential is always measured between two conductors, therefore a reference electrode is used (**Figure 5102.03.02**).

Electrode Potential
Measured by Means of a Reference Electrode



Electrode Potential:

potential difference between electrode and electrolyte

It is only possible to measure a potential difference between two metals

Selection of a reference system:
$2H^+ + 2e^- \Leftrightarrow H_2 \quad E^O_O = 0$

TALAT Training in Aluminium Application Technologies | Electrode Potential Measured by Means of a Reference Electrode | 5102.03.02

The normal hydrogen electrode is used as reference electrode:

$$2H^+ + 2e^- \Leftrightarrow H_2$$

measured with a Pt-electrode in a solution with the following conditions:

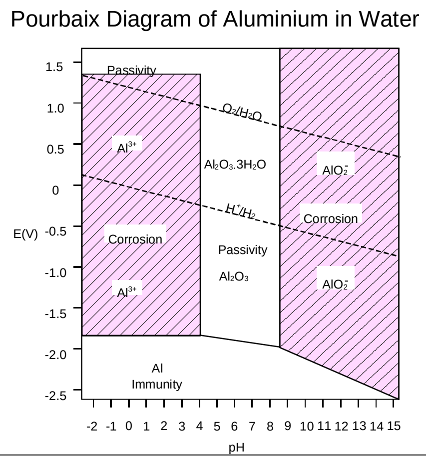
$[H^+] = 1$, $T = 25$ °C, $p_{H_2} = 1$ atm. This system has a potential of 0 V.
A more usual reference electrode is the calomel electrode in a saturated KCl-solution with a potential of + 242 mV against the hydrogen electrode.

For Al two important standard Nernst potentials can be found:

$Al \rightarrow Al^{3+} + 3e^-$	- 1,7 V	Al^{3+} production
$Al + 4OH^- \rightarrow H_2AlO_3^- + H_2O + 3e^-$	- 2,35 V	Aluminate ion production

As these potentials are very negative it can be concluded that Al is a very unnoble metal. Of course, it must be considered that Al is always covered by an air-formed/passive film. This oxide layer covers the Al surface and protects it from reaction. In this way aluminium becomes nobler.

5102.04 Pourbaix Diagram



TALAT Training in Aluminium Application Technologies | Pourbaix Diagram of Aluminium in Water | 5102.04.01

Until now we only considered the Al-Al ions (aluminate) equilibrium. However, we should keep in mind that we are considering an aqueous solution containing other ions. The stability of the aluminium surface as a function of pH can be derived from the E-pH diagram, also called Pourbaix diagram (**Figure 5102.04.01**).
Different regions can be noted. At very low potentials we have the immunity regions of Al, meaning that aluminium will not react. At low pH values aluminium is not stable in

aqueous solution and the formation of Al-ions will take place, also at high pH values aluminate anions are formed. Between pH 4 and 8,5 the oxide layer is stable.

5102.05 Driven Processes on the Aluminium Surface

The situation represented in **Figure 5102.03.01** is again considered. The following situations may occur.

- at equilibrium we have the situation which was explained earlier:

$$Al \Leftrightarrow Al^{3+} + 3e^- \qquad E = E_o$$

- in the case of a driven process we may have

oxidation $Al \Rightarrow Al^{3+} + 3e^- \qquad E > E_o$

velocity $zFd[Al3+]/dt = I_{ox} \geq 0$

$J_{ox} = I_{ox}/ S$

reduction $Al \Leftarrow Al^{3+} + 3e^-$ is not possible in water
(see Pourbaix Diagram)

$2H^+ + 2e^- \Rightarrow H_2 \qquad E < E_o$

velocity $zFd[H_2]/dt = I_{red} \leq 0$

$J_{red} = I_{red}/S$

where J is the current density, I is the current and S is the electrode surface area. To force the reaction in a direction the electrode potential must be positive or negative.

$$E = E_o + \eta$$

where
E = galvanic potential
E_o= the Nernst potential and
η = overpotential

The rate of an electrochemical reaction is given by

$$O + ze^- \Leftrightarrow R$$

$$v_{ox} = 1/S \cdot d[R]/dt$$
$$v_{red} = 1/S \cdot d[O]/dt$$

where

v_{ox} = oxidation rate;
v_{red} = reduction rate and
S = electrode surface area

$$1/zS \cdot dQ/dt = I/S = J$$

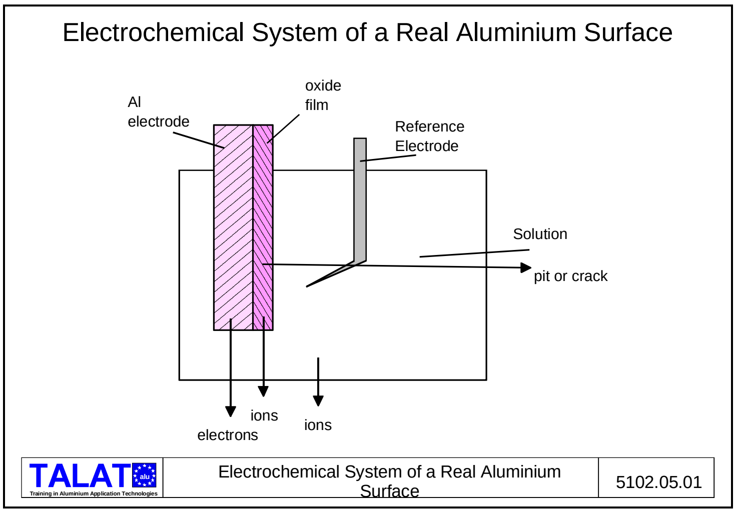
Q = charge passed;
I = current;
J = current density.

By convention the current is taken positive or negative when

$$\eta > 0 \quad J \geq 0$$
$$\eta < 0 \quad J \leq 0$$

The polarization curve gives the relation between the current and the electrode potential. Important information can be gained: the rate determining step; charge transfer, mass transfer or other important steps. The theory of the polarization curve and its interpretation can be found in several electrochemistry books.

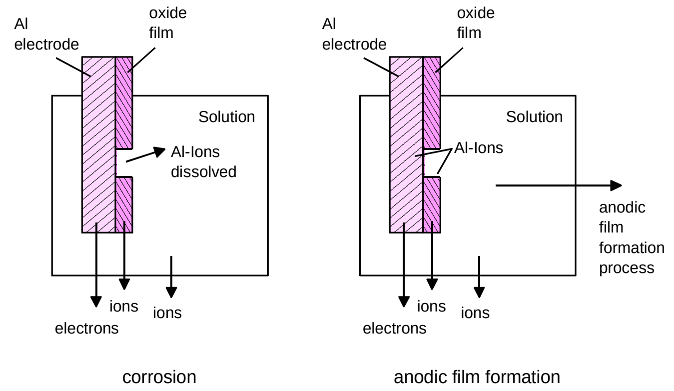
If we consider the polarization behaviour of aluminium in different electrolytes it is important to come to the situation of the real Al surface (model 3, **Figure 5102.02.01**). The aluminium surface is polarized positively, $E > E_o$, the reaction: $Al \Rightarrow Al^{3+} + 3e^-$ with a current $I_{ox} = J_{ox}S'$ will occur at some places (in the pit or crack, see **Figure 5102.05.01**).


Electrochemical System of a Real Aluminium Surface

Electrochemical System of a Real Aluminium Surface 5102.05.01

At that moment the fate of the Al-ions becomes very important. This fate is completely related to the chemistry of the aluminium in the solution in the neighbourhood of the pit or crack. There are now two possibilities: either the solution is repairing the crack, the surface is repassivated or the aluminium ions are easily dissolved into the electrolyte (see **Figure 5102.05.02**) and a pit will be formed.

Difference in Anodic Behaviour of the Aluminium Due to the Fate of the Al-Ions



TALAT | Difference in Anodic Behaviour of the Aluminium Due to the Fate of the Al-Ions | 5102.05.02

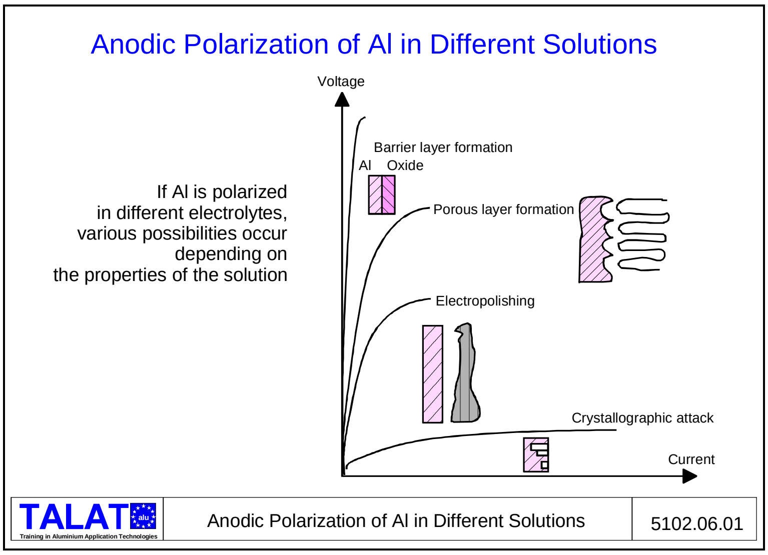
5102.06 Anodic and Cathodic Polarization of Al in Different Solutions

Anodic

From the previous discussion it becomes clear that if Al is polarized anodically in different solutions, various possibilities occur depending on the properties of the solution. **Figure 5102.06.01** shows a schematic representation of the different polarization curves which may be obtained.

The difference in anodic behaviour can be briefly explained as follows:

1. The oxide film is largely insoluble ⇒ barrier layer formation mechanism is based on ionic migration ⇒ high potential drop across the barrier layer.
2. The oxide film is sparingly soluble ⇒ porous oxide film formation barrier layer formation, pore initiation and regular porous oxide film growth.
3. The oxide film is better soluble in the electrolyte ⇒ electropolishing
4. Metal dissolution can compete with oxide film formation ⇒ etching and pitting



Anodic Polarization of Al in Different Solutions

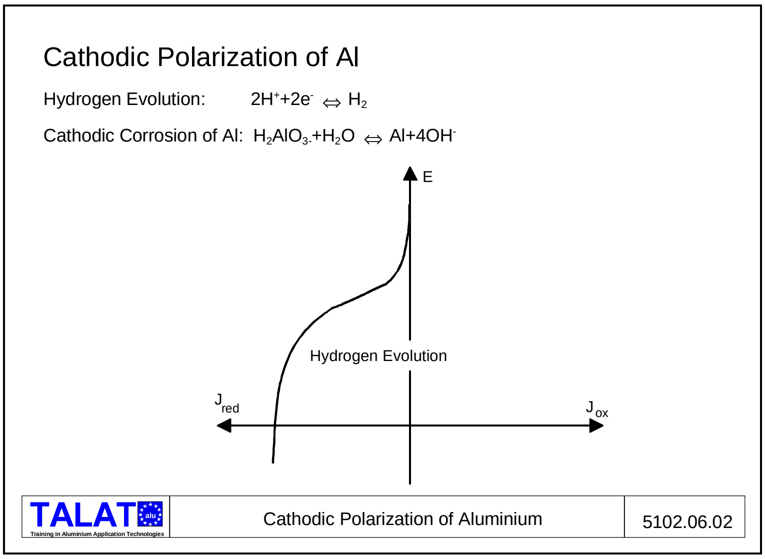
If Al is polarized in different electrolytes, various possibilities occur depending on the properties of the solution

TALAT Training in Aluminium Application Technologies | Anodic Polarization of Al in Different Solutions | 5102.06.01

Cathodic

If aluminium is polarized cathodically in aqueous solutions, hydrogen evolution results (**Figure 5102.06.02**). This may lead to cathodic corrosion of the aluminium according to the reaction:

$$H_2AlO_3^{\,-} + H_2O \Leftrightarrow Al + 4OH^{\,-} .$$



Cathodic Polarization of Al

Hydrogen Evolution: $2H^+ + 2e^- \Leftrightarrow H_2$

Cathodic Corrosion of Al: $H_2AlO_3^- + H_2O \Leftrightarrow Al + 4OH^-$

TALAT Training in Aluminium Application Technologies | Cathodic Polarization of Aluminium | 5102.06.02

5102.07 Internal and External Polarization of the Aluminium Surface

It is important to realize that in order to have an electrochemical reaction on the aluminium surface an overpotential must be created on the aluminium surface. The aluminium electrode can be polarized anodically or cathodically as was shown in section **5102.06**.

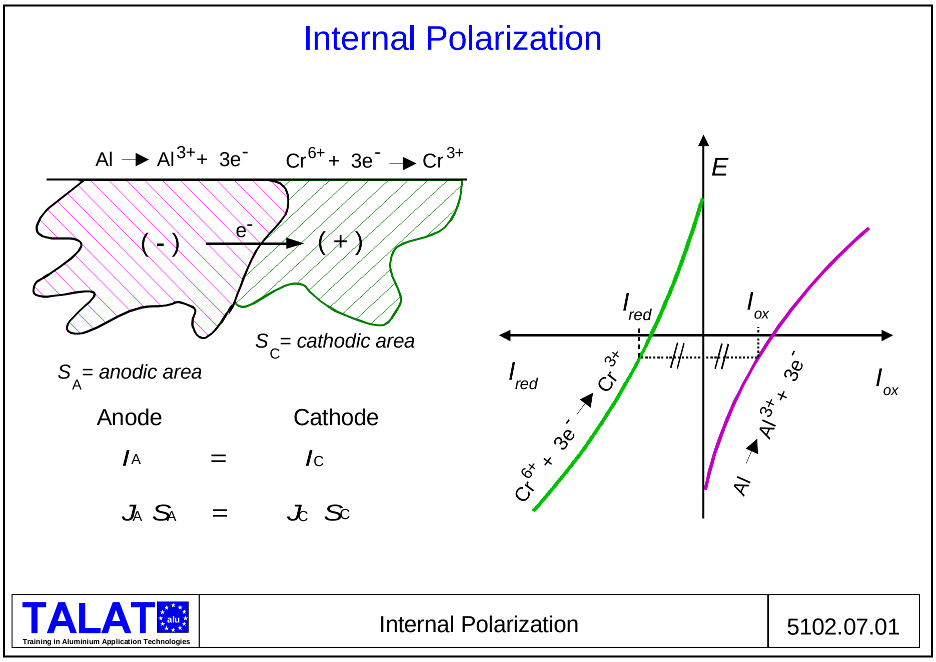
We will make two distinctions:
the first is the case where an external power source is used to polarize the aluminium surface positively or negatively. This will be called external polarization. If we consider now the surface treatment processes on aluminium, numerous examples can be given where during the treatment process an external power source is used to drive the aluminium surface anodically or cathodically. Examples are given below. The lectures that will deal with this case are also indicated.

External Polarization	Surface Treatment	TALAT Lecture
positively (anodically)	anodizing	**5203**
	electrochemical polishing	**5201**
negatively (cathodically)	plating	**5205**
	colouring	**5203**
AC polarization (alternatively positive and negative)	anodizing	**5203**
	AC etching for graining	**5201**
	colouring	**5203**

From the previous section **5102.06** it becomes clear that the composition of the solution and the external polarization (overpotential- current density) will entirely control the treatment process. This behaviour is reflected in the polarization curve as is shown in **Figure 5102.06.01** and **Figure 5102.06.02.**

In the second case, where on the surface spontaneous potential differences occur, will be called internal polarization. Here no external electrical power source exists, but locally the aluminium electrode becomes anodic or cathodic. This can occur for various reasons, e.g. a difference in composition of the aluminium (as was indicated in **TALAT Lecture 5101**). It is important to realize that locally the same polarization curve applies (**Figure 5102.06.01** and **Figure 5102.06.02)**. However, we must consider anodic and cathodic areas on the surface where oxidation and reduction reactions take place with equal total current.

Simplified, this situation is explained in **Figure 5102.07.01.** Consider a conversion process where Cr^{6+} is reduced by the oxidation of Al. At some places the aluminium is positive where the reduction of Cr^{6+} will take place. At other places the aluminium surface is negative where the oxidation takes place. If anode and cathode are in electrical contact with each other, a current *I* will flow, leading to a reduction of Cr^{6+} and an oxidation of the aluminium. The anodic and cathodic current must be equal as can be seen in the polarization curve. From this it can be concluded that the anodic and cathodic areas become important. So the system will be completely controlled by local electrochemistry. If we come now to **TALAT Lectures 5100 and 5200** numerous examples can be given where the aluminium surface is polarized internally.


Internal Polarization

Internal Polarization

5102.07.01

Internal Polarization	**TALAT Lecture**
corrosion processes	**5103**
chemical polishing	**5201**
chemical etching	**5201**
conversion coatings	**5202**
electroless plating	**5205**

5102.08 Literature

Electrochemistry

Bard, A. and **Faulkner, L.:** “Electrochemical Methods“, John Wiley Sons, 1980
Vetter, K.:“Electrochemical Kinetics“, Academic Press, 1967

Corrosion

Kaesche, H.: “Metallic Corrosion“, NACE, 1985
Scully, J.C.: “Corrosion: Aqueous Processes and Passive Films“, Academic Press, 1983
Szklarska-Smialowska, Z.: “Pitting Corrosion of Metals“, NACE, 1986

5102.09 List of Figures