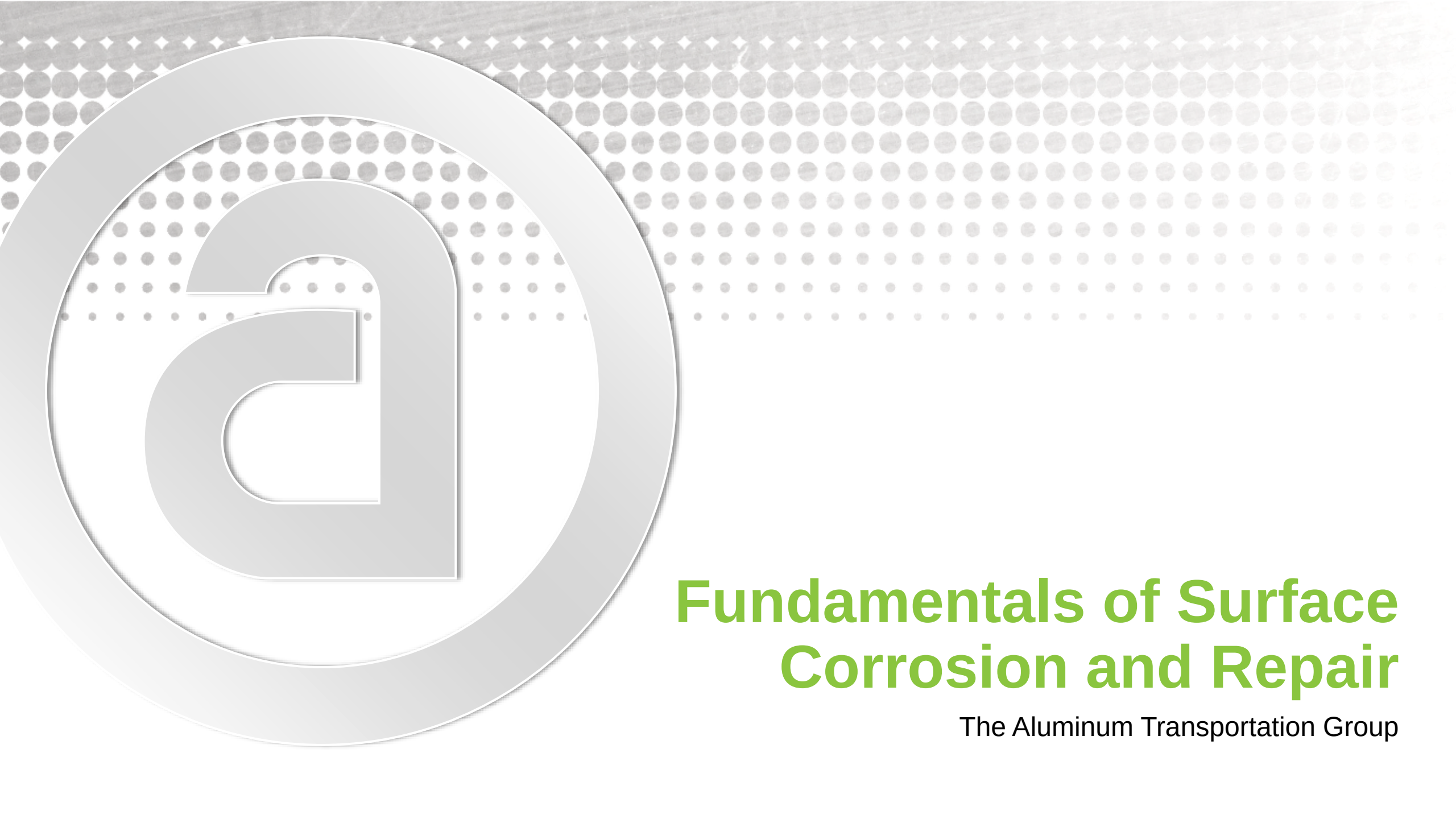




Fundamentals of Surface Corrosion and Repair

The Aluminum Transportation Group

Presenter

Tamer O. Girgis, Ph.D.

Aleris

*Surface Treatment R&D/Sr.
Applications Engineering*



Outlines of Surface Technology Course

- Introduction
- Objective
- Importance of aluminum surface technologies
- Impact of corrosion in automotive
- Surface influence on several automotive applications and in-service performances
- Factors determining rate of corrosion
- Typical forms of corrosion in automotive body sheets
- Sources of oxidation in aluminum processing
- Methods to control and improve surface quality of aluminum
- Influence of pretreatment on adhesive bonding in automotive joints
- Repair of aluminum panels and BIW parts

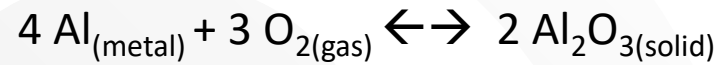
Impact of Corrosion



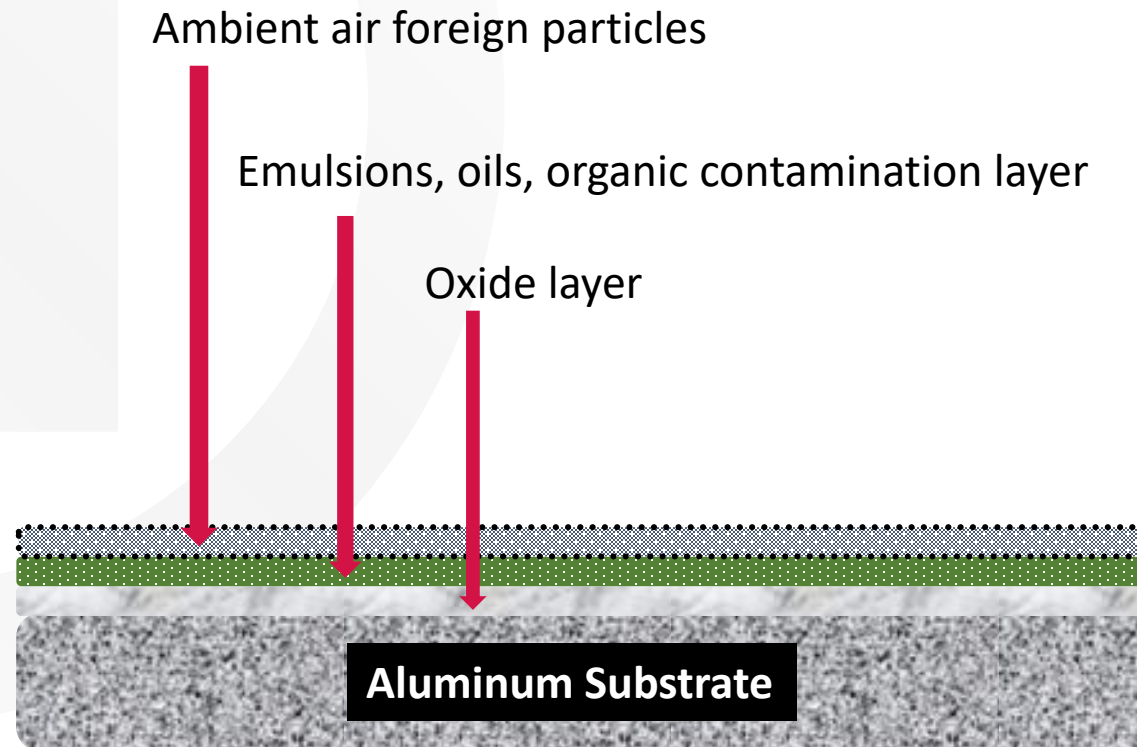
Courtesy of Richard Griffin

Aluminum Surface

Aluminum is naturally coated with a protective layer, or passivation layer. It is an oxide layer formed according to the reaction:



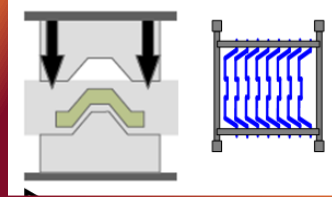
The very high reactivity of aluminum is due to a high value of free energy (-1675 kJ).



As produced aluminum substrate

Surface Influence

Surface has influence on several applications and in-service performance



Stamping



- Stamping/die wear



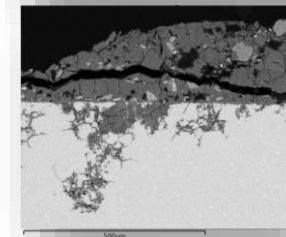
Assembly



- Adhesive bondability
- Welding/electrode wear



In-Service



- Corrosion

Outline

Understanding Corrosion

Surface Oxidation in Aluminum

Surface Coating Technologies

Adhesive Bonding

Repair of Aluminum Panels and BIW Parts

Outline

Understanding Corrosion

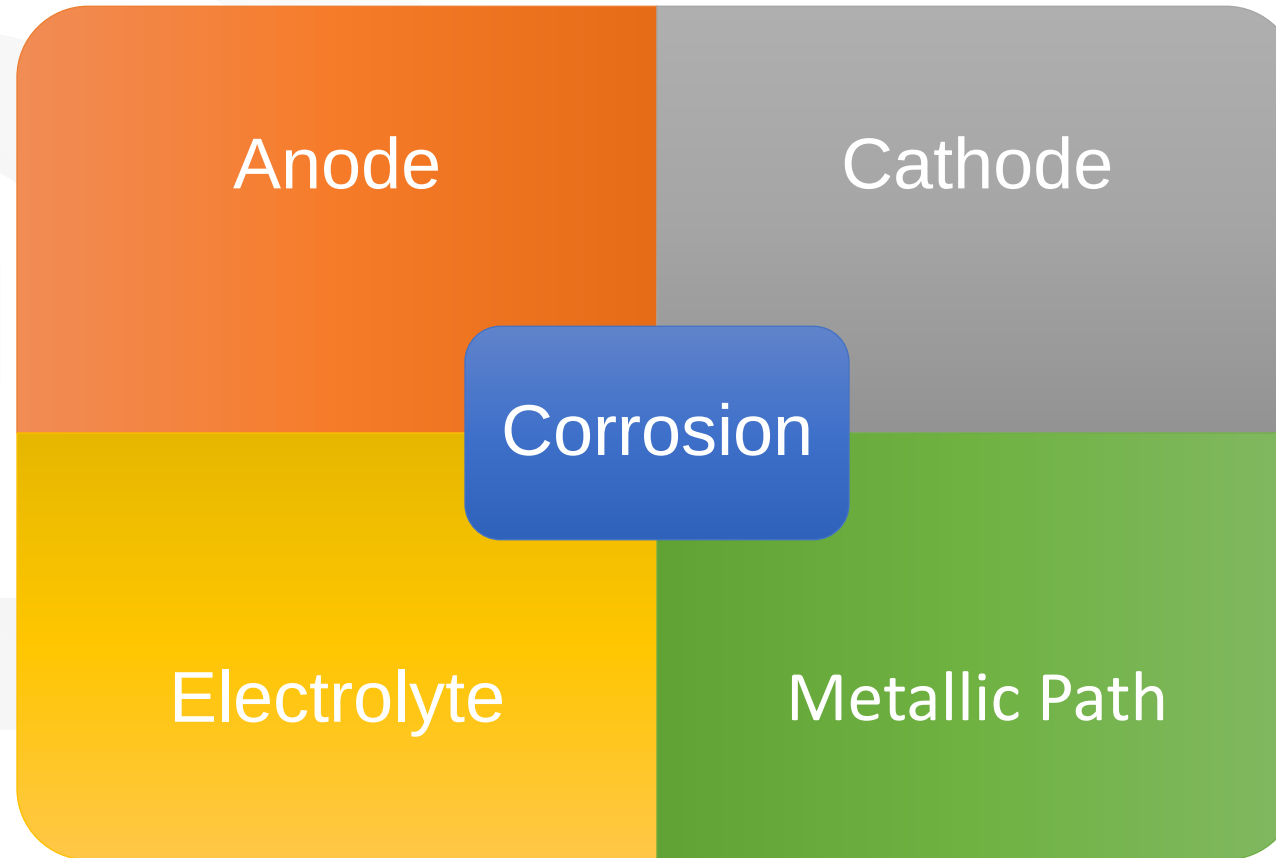
Surface Oxidation in Aluminum

Surface Coating Technologies

Adhesive Bonding

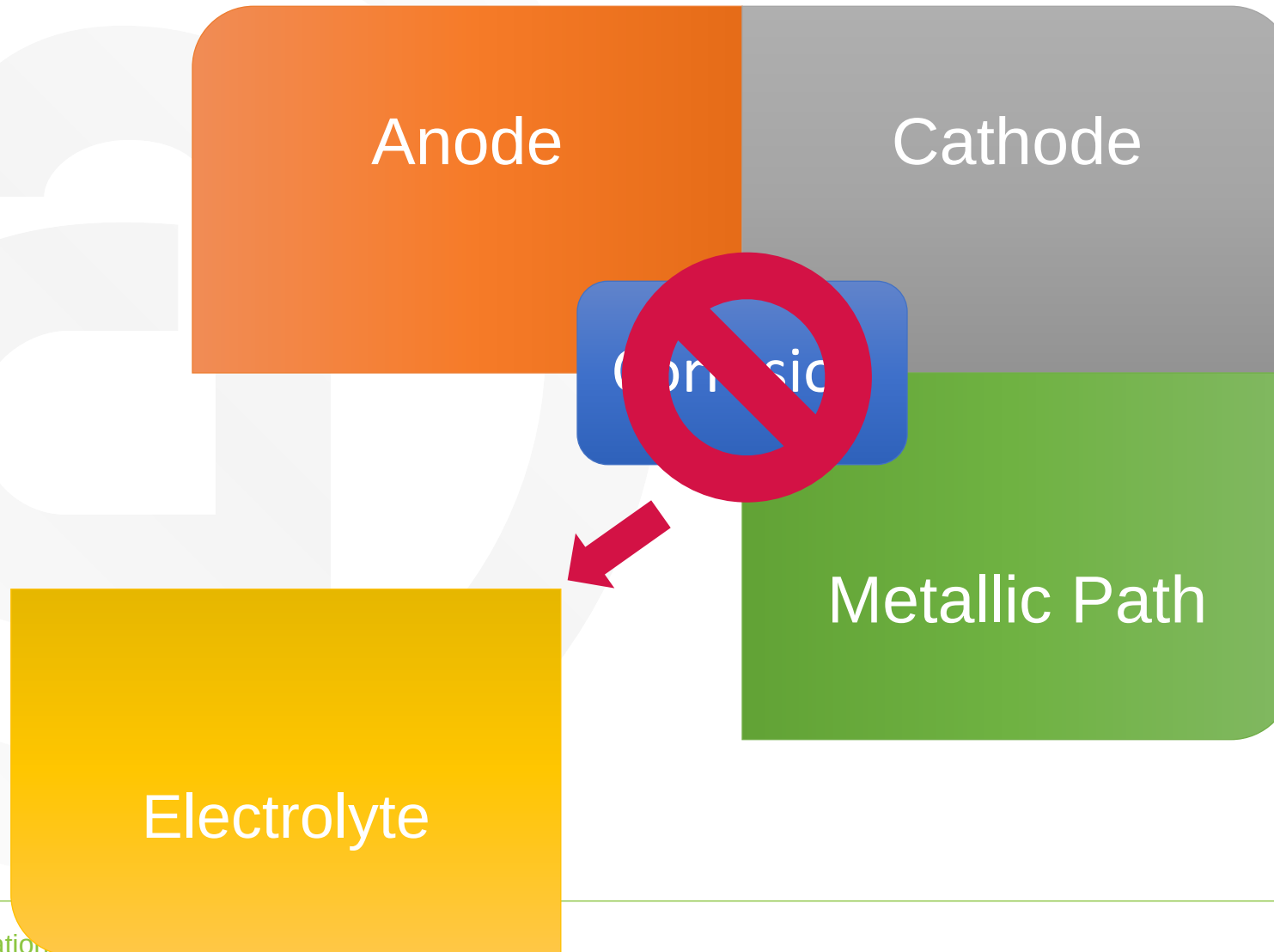
Repair of Aluminum Panels and BIW Parts

Corrosion Puzzle

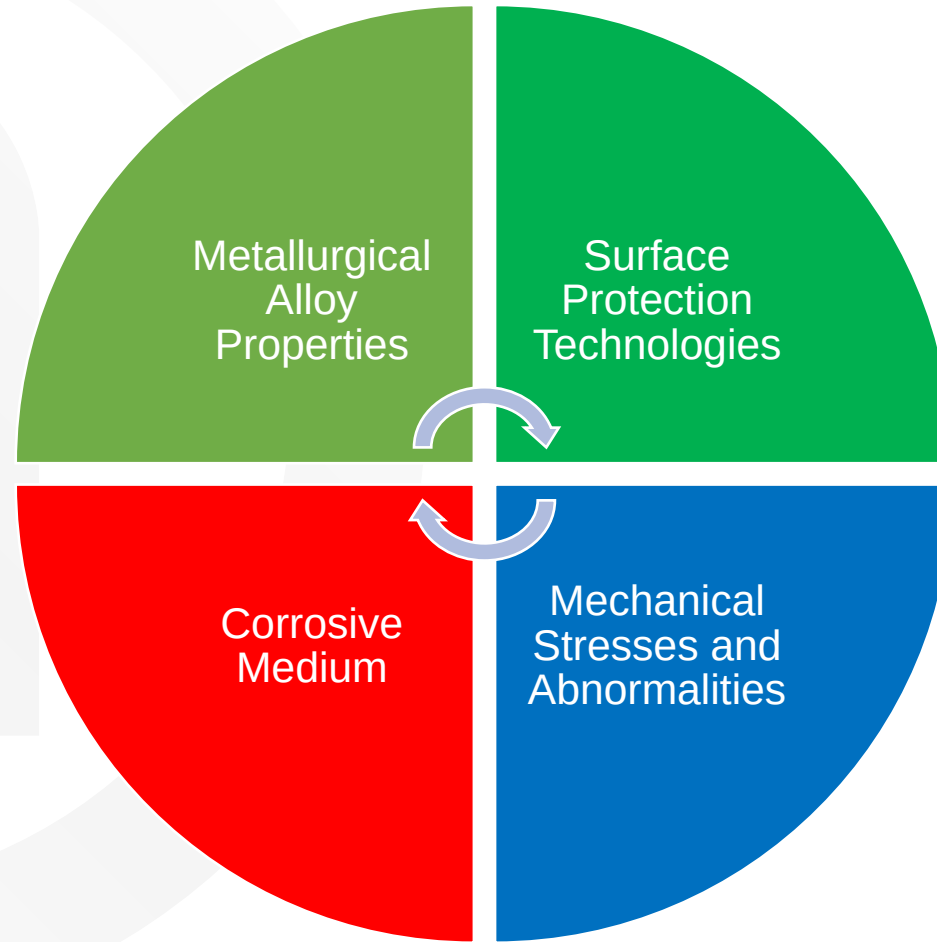


(4 Requirements)

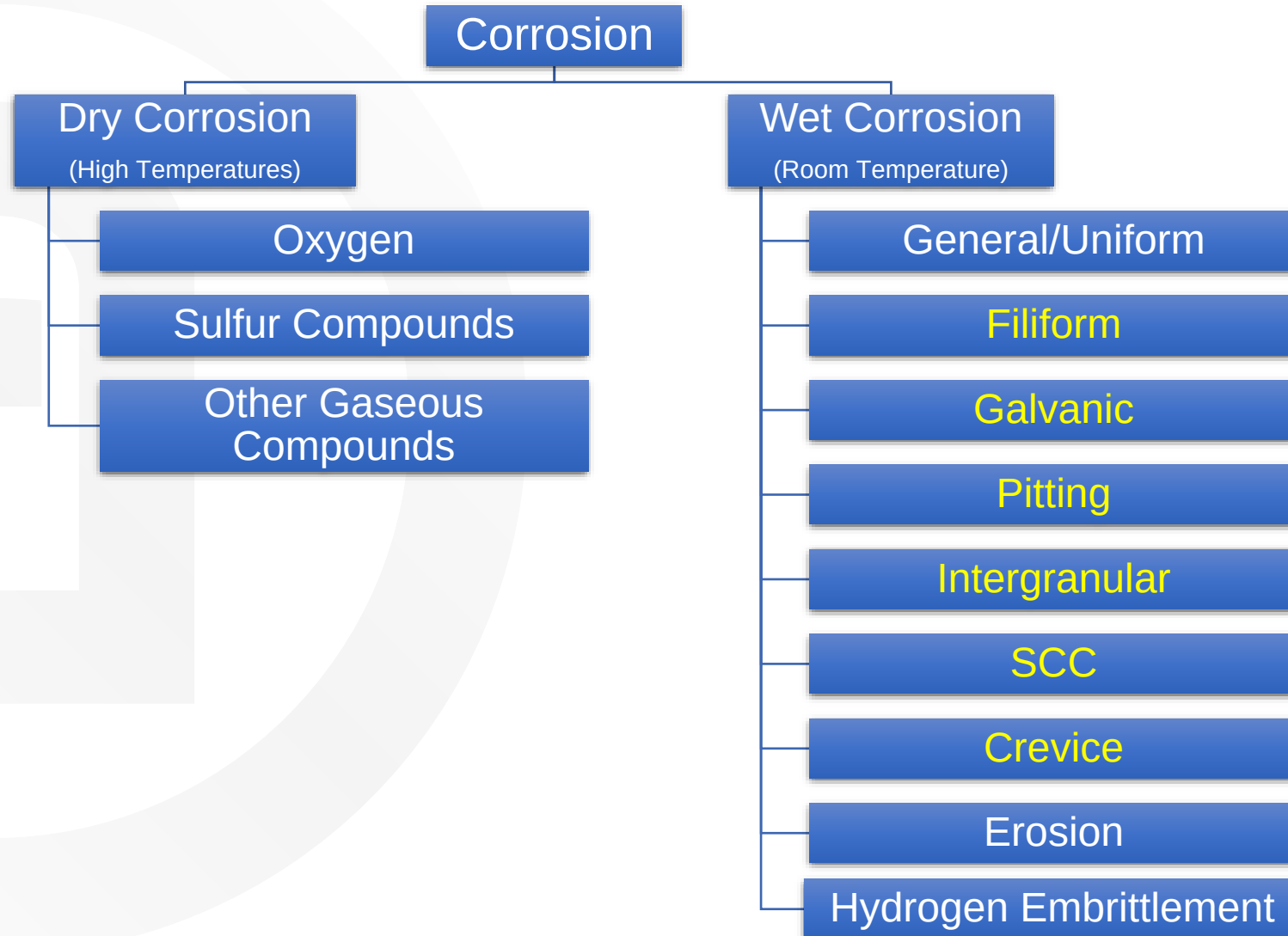
Corrosion Puzzle



Factors Determining Rate of Corrosion

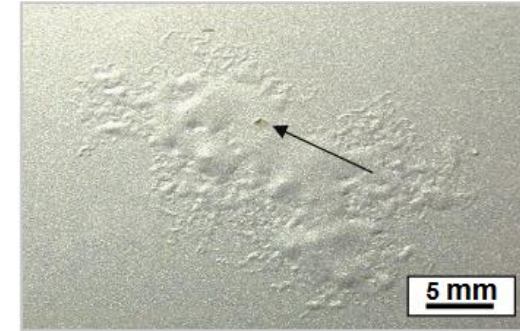
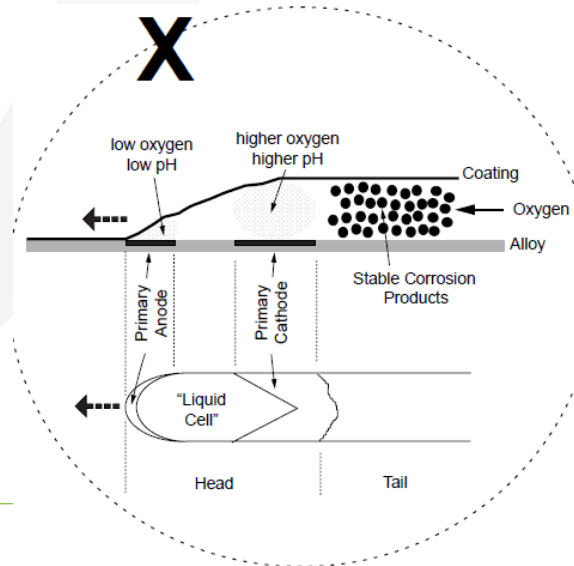
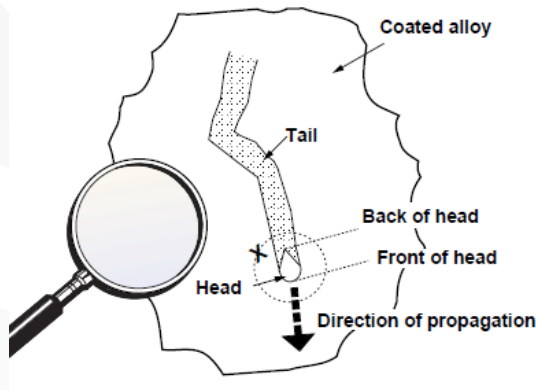


Forms of Corrosion



Filiform (Cosmetic) Corrosion

- Self propagating **crevice corrosion**
- Localized form of corrosion that occur under the coating or paint
- Steel, aluminum and other alloys are affected
- “Wormlike” visual appearance



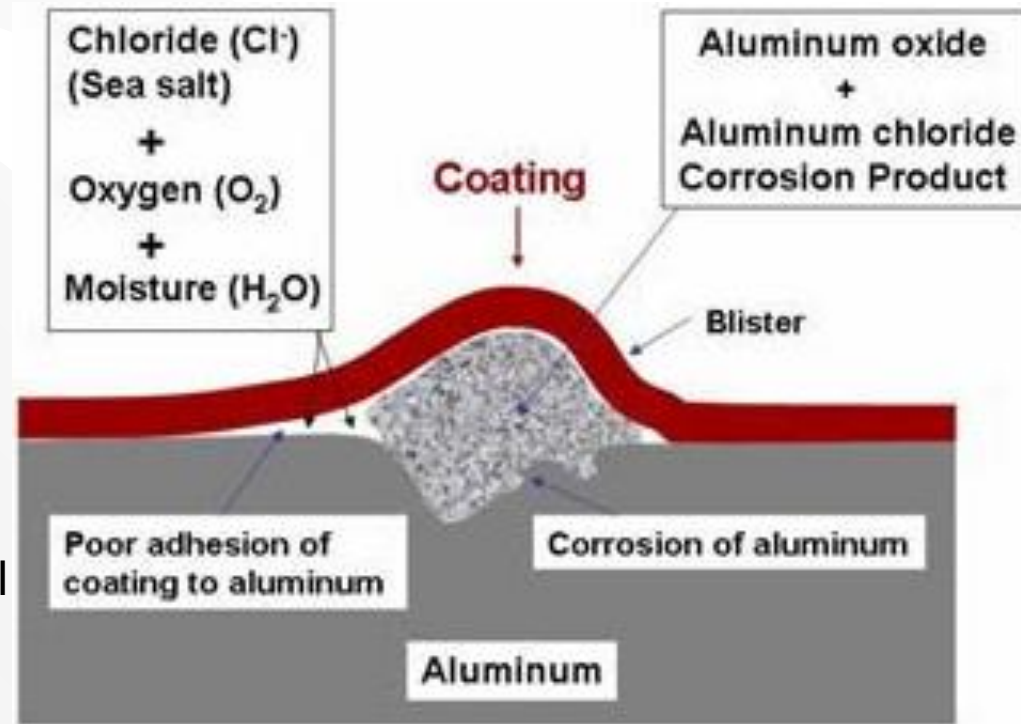
Source: G M Scamans, A. Afseth, G E Thompson, J Liu and X Zhou, "Aluminum Automotive Closure Sheet Corrosion"

Filiform (Cosmetic) Corrosion



Solution in Automotive body sheets:

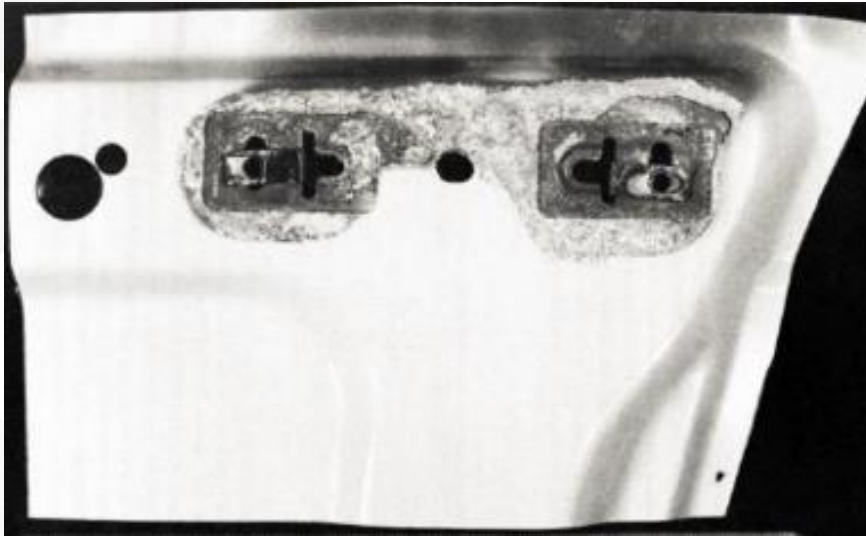
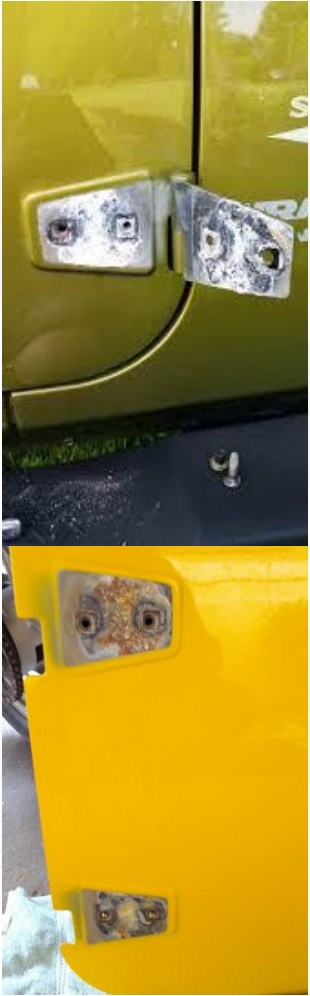
It is recommended to limit the use of rectification by mechanical grinding prior to vehicle painting



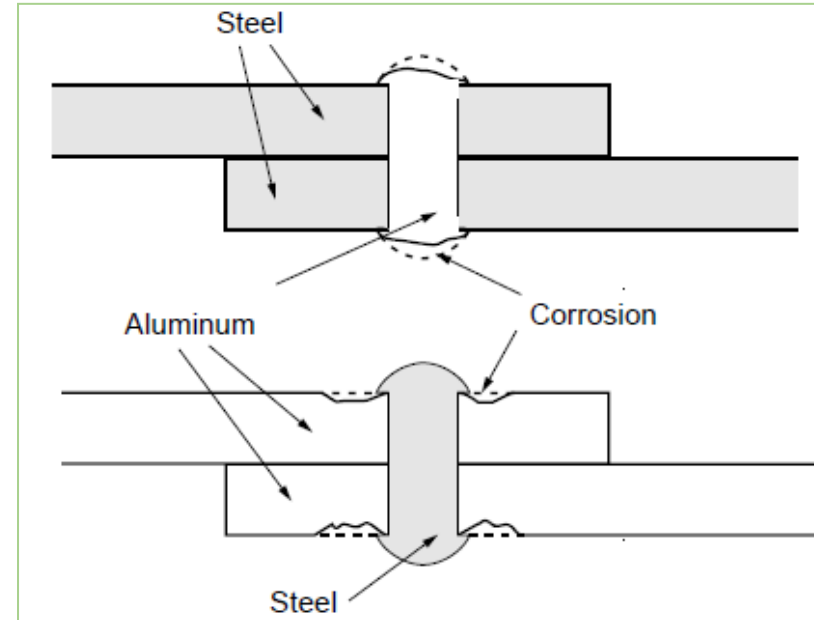
Preventative measures for filiform corrosion:

- Thoroughly cleaning the surface prior to coating
- Applying OEM recommended corrosion protection
- Eliminating surface abnormalities (e.g., pores, mechanical damage, insufficient coverage, etc.)
- Applying OEM recommended refinish materials

Galvanic Corrosion



Aluminum Sheet Coupled with Steel
A steel member (not shown in the picture), approximately the size and shape of the corroded region, was in contact with the aluminum sheet



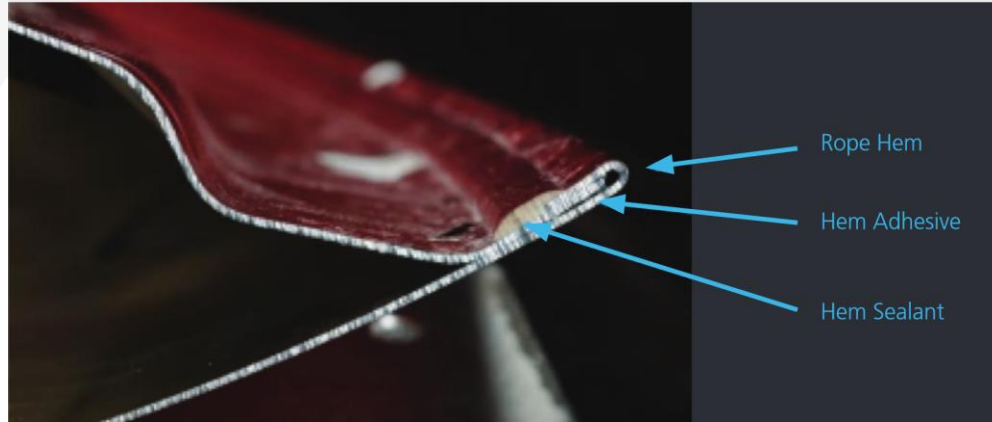
Electromotive Force Series (Galvanic Series)

Prevention of Galvanic Corrosion:

- Avoid combinations in which the area of the less noble material is relatively small.
- Insulate dissimilar metals via robust coatings.
- Use coated steels (EG, GA,...etc.) in contact with aluminum
- Use OEM recommended coated fasteners
- Select proper Insulating washers if specified to electrically isolate components
- At high risk corrosion areas use Sealants, such as adhesives, primers, and other refinish coatings for corrosion prevention between dissimilar metals

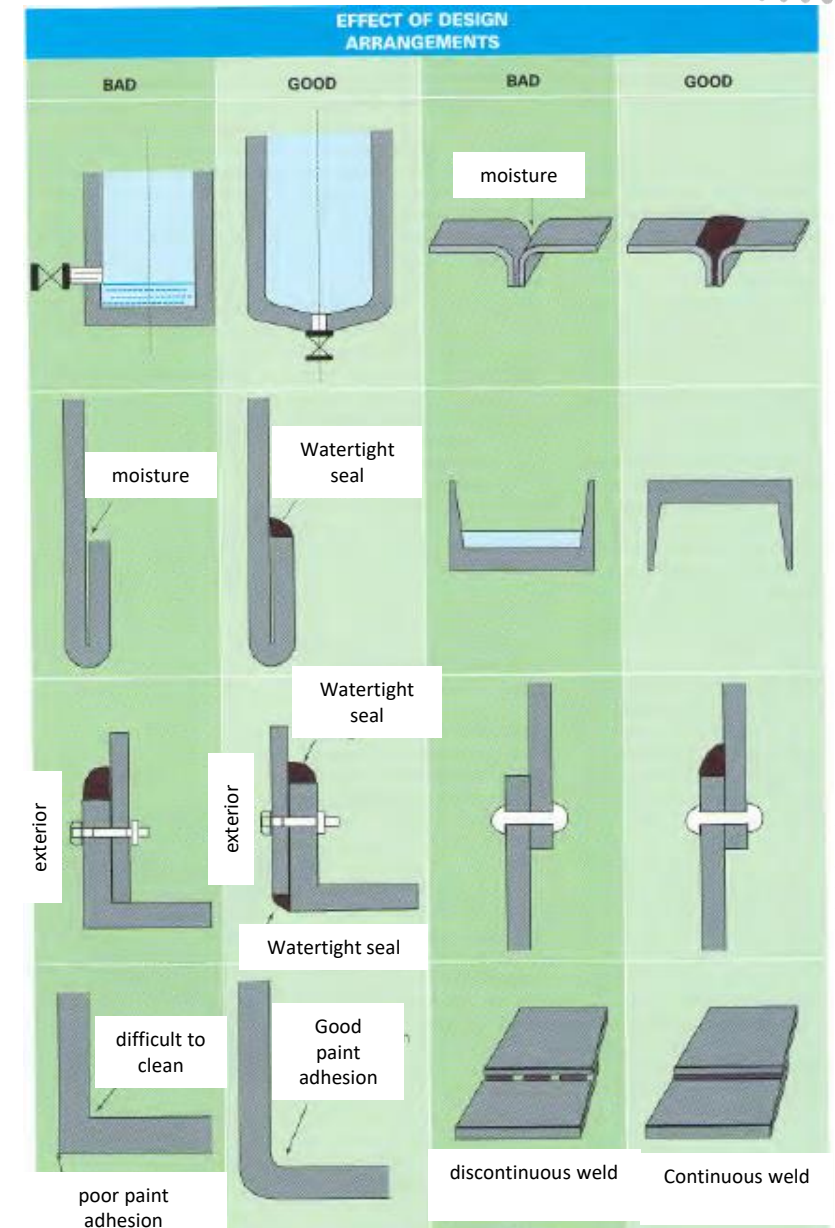
Electrode reaction	Standard potential at 25 °C (77 °F), V-SHE	
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	1.50	Noble metals ↑
$\text{Pd}^{2+} + 2e^- \rightarrow \text{Pd}$	0.987	
$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	0.854	
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.800	
$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$	0.789	
$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	0.521	↓ Active metals
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.337	
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000 (Reference)	
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126	
$\text{Sn} + 2e^- \rightarrow \text{Sn}$	-0.136	
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250	
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.277	
$\text{Tl}^+ + 2e^- \rightarrow \text{Tl}$	-0.336	
$\text{In}^{3+} + 3e^- \rightarrow \text{In}$	-0.342	
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.403	
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440	
$\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}$	-0.53	
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.74	
$\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$	-0.91	
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763	
$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18	
$\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$	-1.53	
$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.63	
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66	
$\text{Hf}^{4+} + 4e^- \rightarrow \text{Hf}$	-1.70	
$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.80	
$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.85	
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37	
$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71	
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87	
$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93	
$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05	

Design Consideration for Corrosion



Avoid:

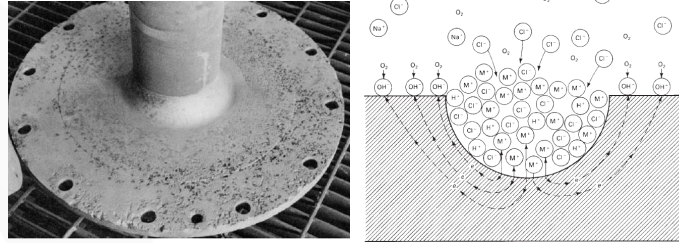
- Regions where water/dust can collect and stagnate
- Sharp corners – difficult to protect
- Sharp internal corners – difficult to clean



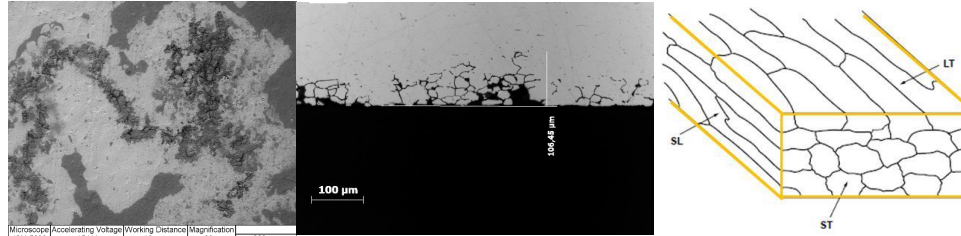
Aluminum Advantages

Types of corrosion more common in steel rather than in aluminum

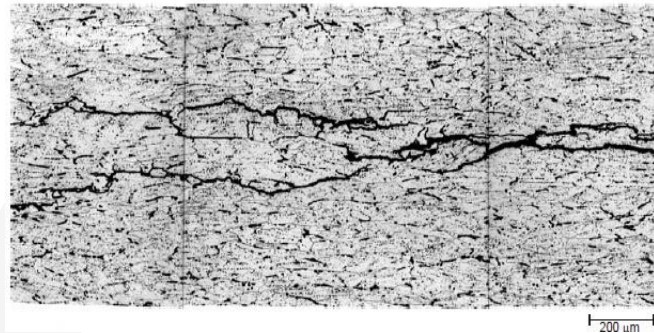
PITTING CORROSION



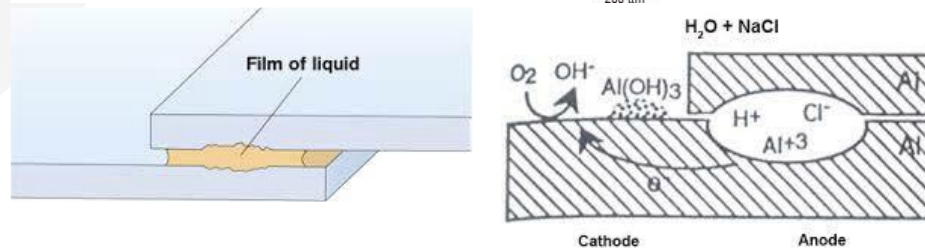
INTERGRANULAR CORROSION



STRESS CORROSION CRACKING

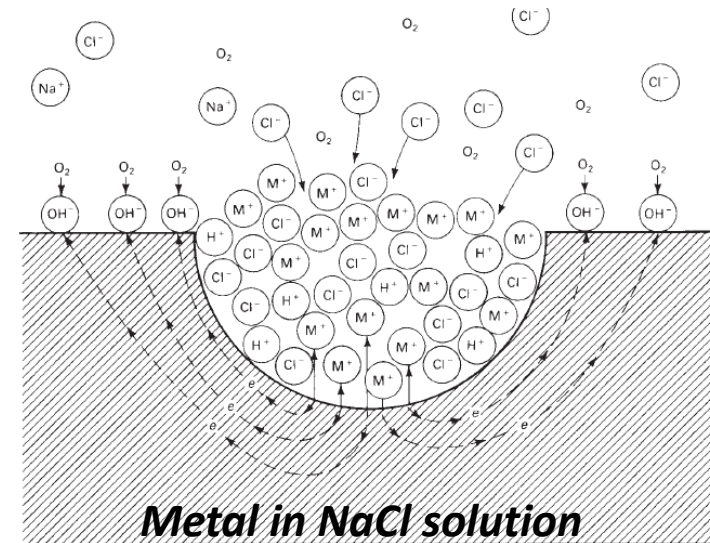
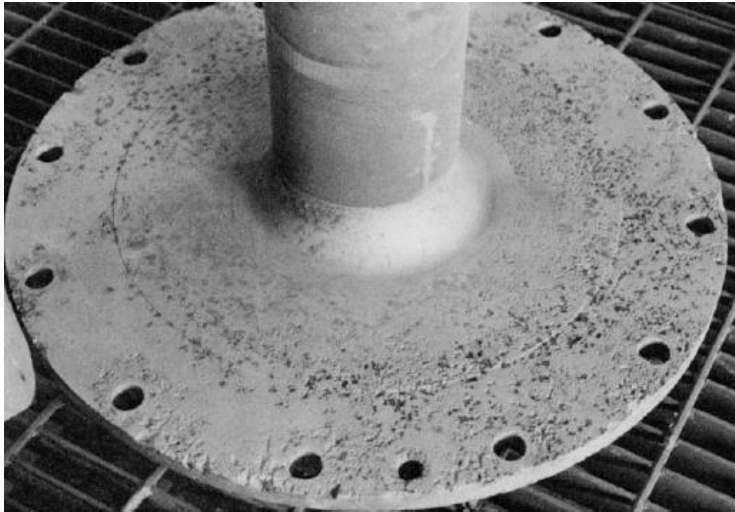


CREVICE CORROSION

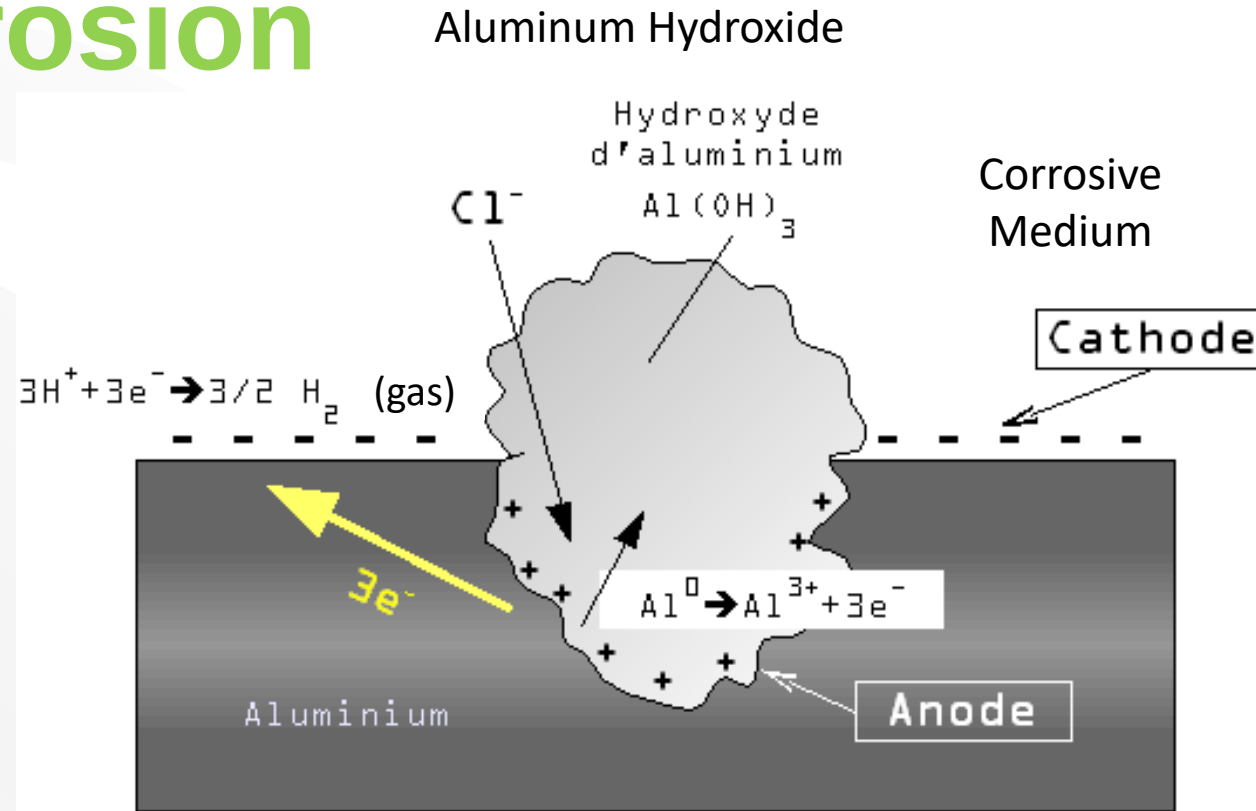


Pitting Corrosion

- Highly localized form of corrosion
- Causes from local inhomogeneity on metal surface, local loss of passivity, rupture of protective oxide coating
- Produce sharp holes (small or large in diameter)
- Examples: metals in contact with acids (*deep pits*), metals immersed in seawater



Pitting Corrosion



- Bare aluminum becomes an anode in which the following oxidation reaction occurs:

$$2 Al \rightarrow 2 Al^{3+} + 6e^-$$
- At the cathode on the surface of the metal, we have the following reactions:

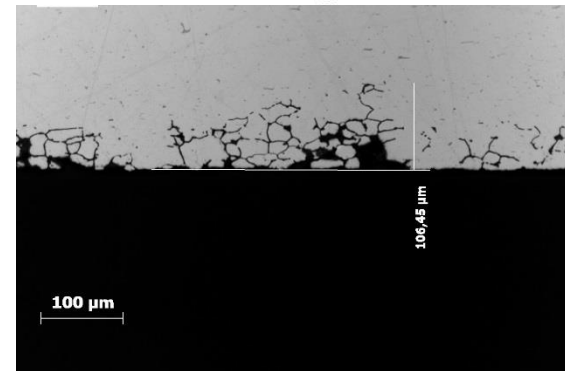
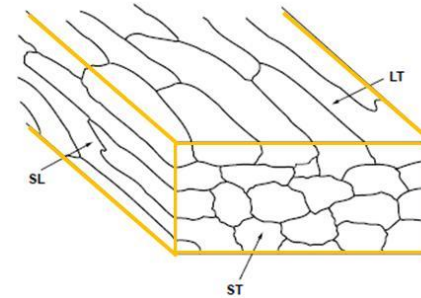
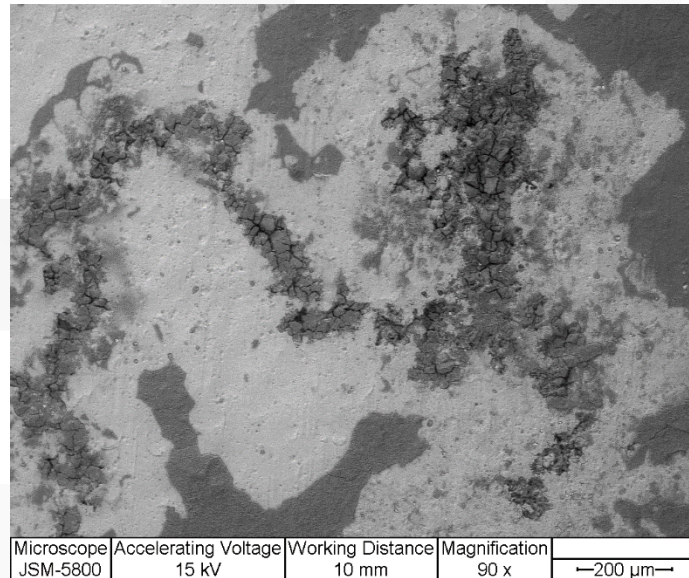
$$3O_2 + 6 H_2O + 12e^- \rightarrow 12 OH^-$$

$$6H^+ + 6e^- \rightarrow 3 H_2$$
- Overall, aluminum metal dissolves to form aluminum hydroxide

$$4Al + 6 H_2O + 3 O_2 \rightarrow 4 Al(OH)_3$$

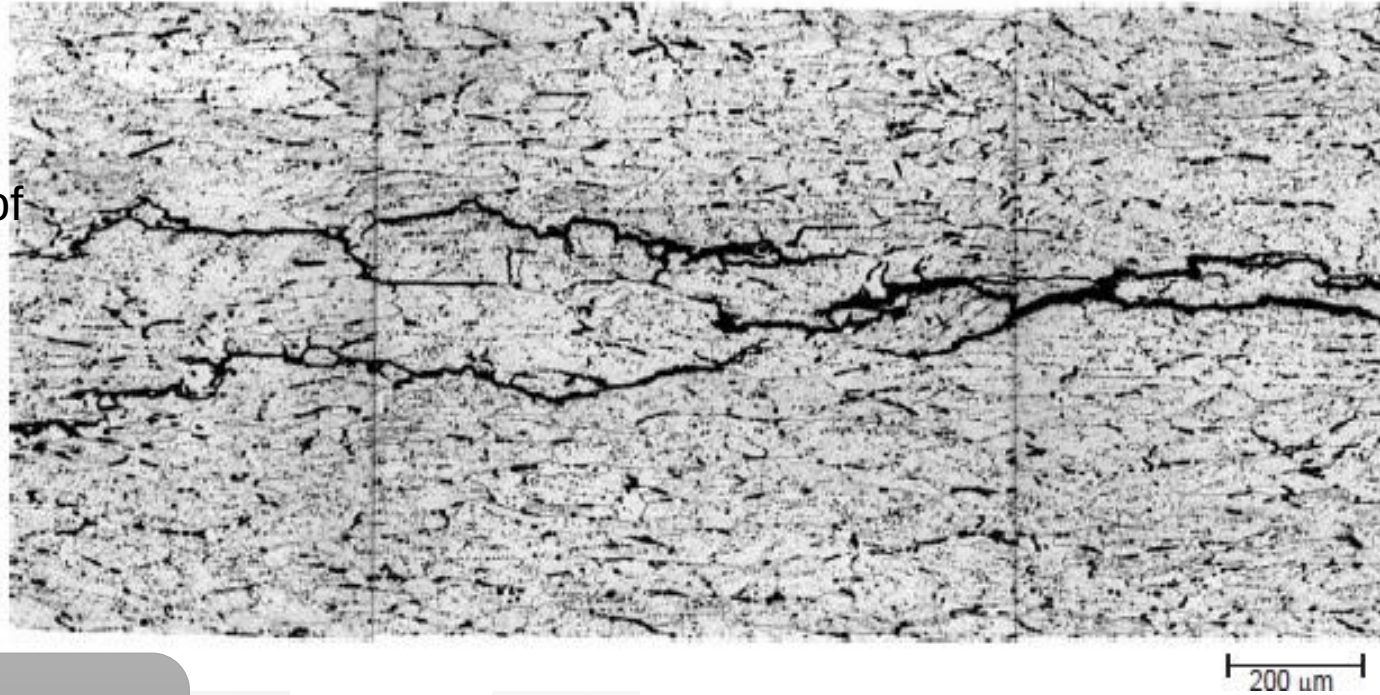
Intergranular Corrosion

- Localized type of attack at the grain boundary of metal
- Grain boundary (small in area) acts as anode
- Rest of the grain (larger area) acts as cathode
- Attack penetrates deeply into the metal

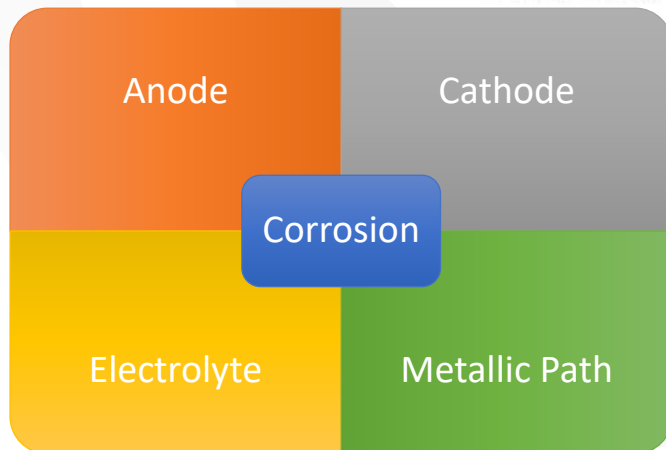


Stress Corrosion Cracking (SCC)

7xxx series aluminum alloys that contain appreciable amounts of soluble alloying elements primarily copper, magnesium, silicon, and zinc, are susceptible to stress corrosion cracking (SCC).



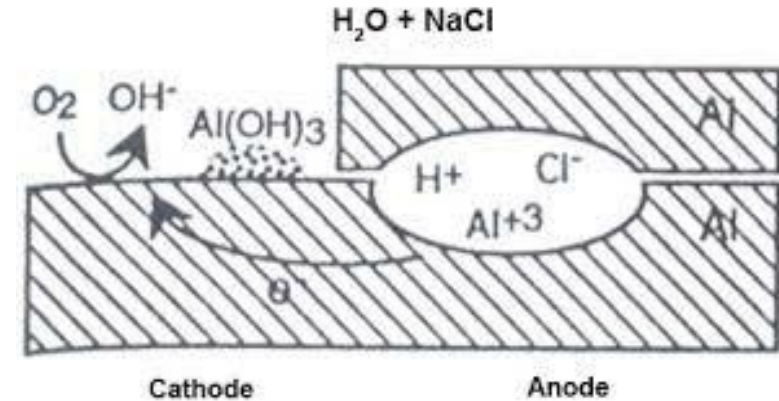
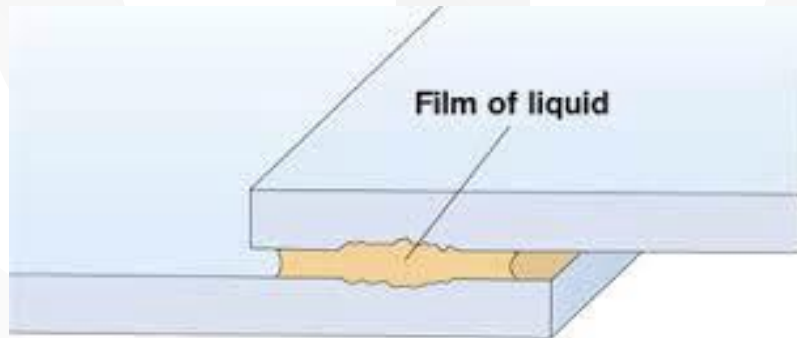
The SCC mode is crack initiation at the junctions of grain boundaries with specimen surface, and crack propagation along grain boundaries into the specimen, attributed to hydrogen embrittlement and anodic dissolution.



- Metal subject to constant tension & exposed simultaneously to a corrosive environment
- Compressive stress is not damaging
- Normally mitigated by certain heat treatment

Crevice Corrosion

- Occur in a joint in contact with another material when a corrosive liquid (salt water) is present between the two surfaces in contact
- Crevices (narrow openings) at mating surfaces can collect and retain moisture that may lead to corrosion
- The mating surfaces can be aluminum to aluminum, aluminum to steel, or aluminum to plastics



Crevice Corrosion factors:

- Higher temperatures and salt content can accelerate the corrosion rate
- It can be found under gasket fittings, welded lap joints, overlapping metal seams, folded or formed sheet hems

Crevice corrosion preventative measures:

- Use techniques and designs that eliminate or seal crevices, to reduce the risk of crevice corrosion
- Corrosion resistant primers, sealers and other refinish materials on aluminum surfaces
- Seam sealers to prevent water entry into joint

Outline

Understanding Corrosion

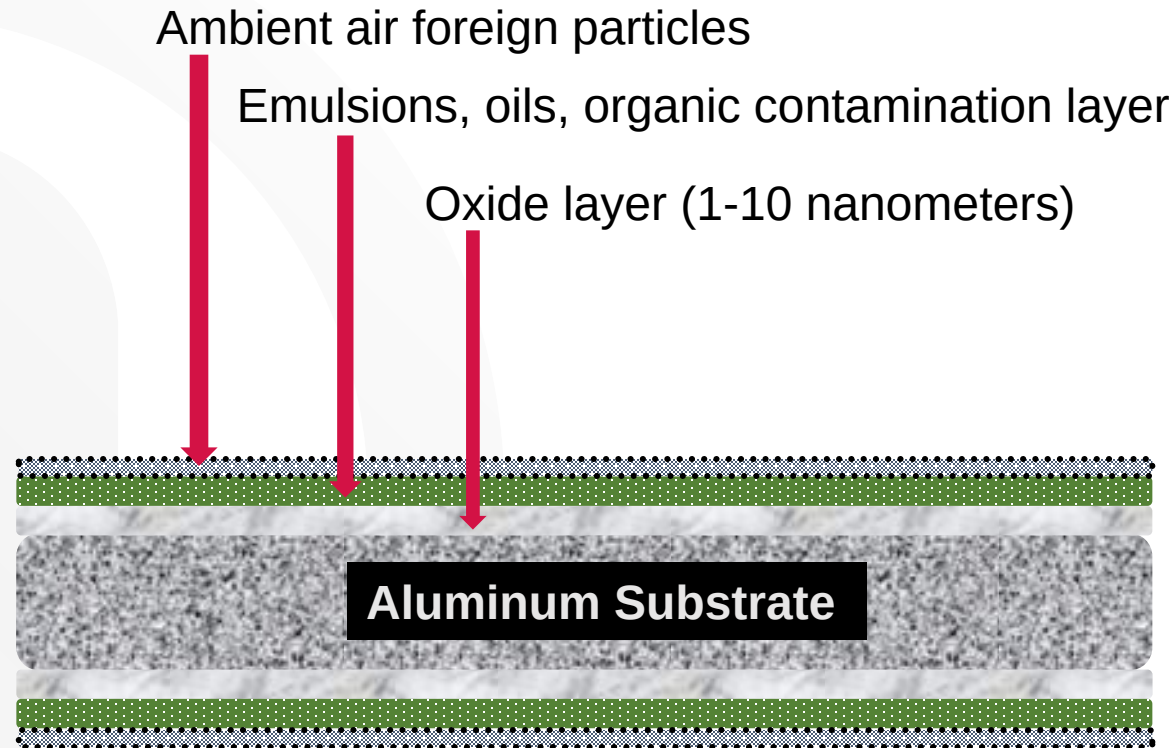
Surface Oxidation in Aluminum

Surface Coating Technologies

Adhesive Bonding

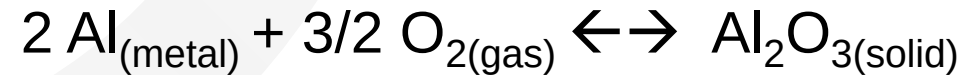
Repair of Aluminum Panels and BIW Parts

Aluminum Surface

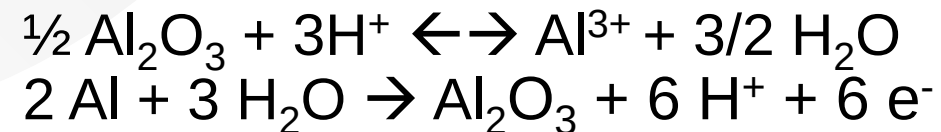


Note: Drawing not to scale.
Just for illustration
purposes

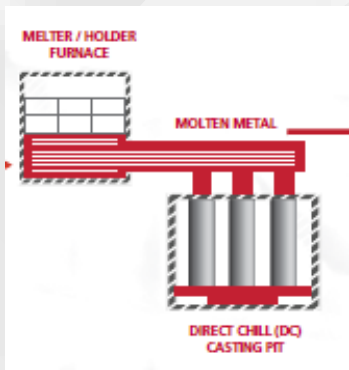
- Generally it is assumed that aluminum reacted with oxygen to form the protective layer as follows:



- Acid solutions affect Aluminum surface properties. Depending on the characteristics of the medium, dissolution of the protective layer or re-passivation of the metal may occur as follows:



Sources of Oxidation in Aluminum Processing



Removal of as cast surface Oxides and inclusions;
the top and bottom surfaces are scalped



Temperature necessary to achieve
recrystallization.
Time & Temp. cycles designed to
achieve metallurgical properties

Hot Working

Soaking Pit



Scalped ingots are loaded into a heating
chamber to achieve uniform homogenization



Annealing



Furnace is used to solution heat treat the
strip to achieve recrystallization.
Furnace employs air flotation systems for
the sheet to prevent abrasion and scratches

Outline

Understanding Corrosion

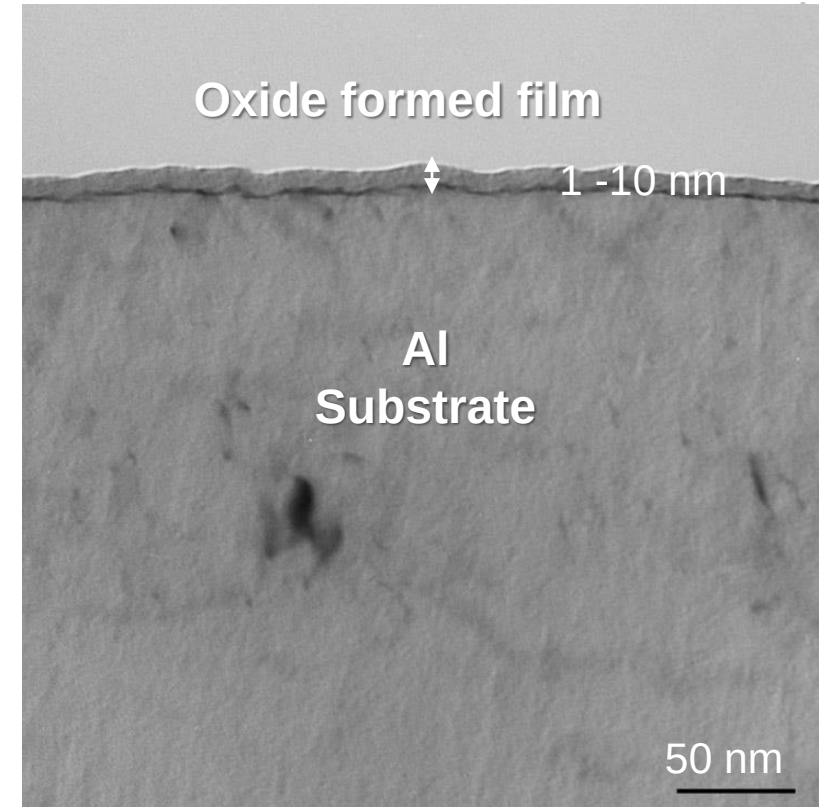
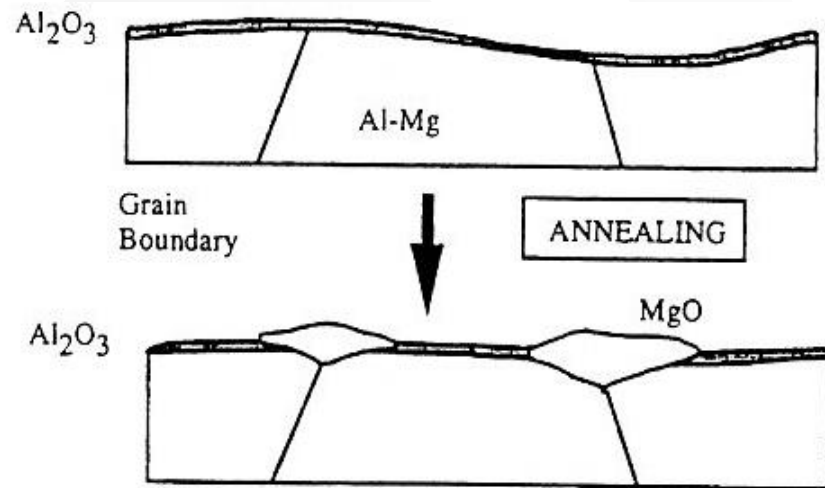
Surface Oxidation in Aluminum

Surface Coating Technologies

Adhesive Bonding

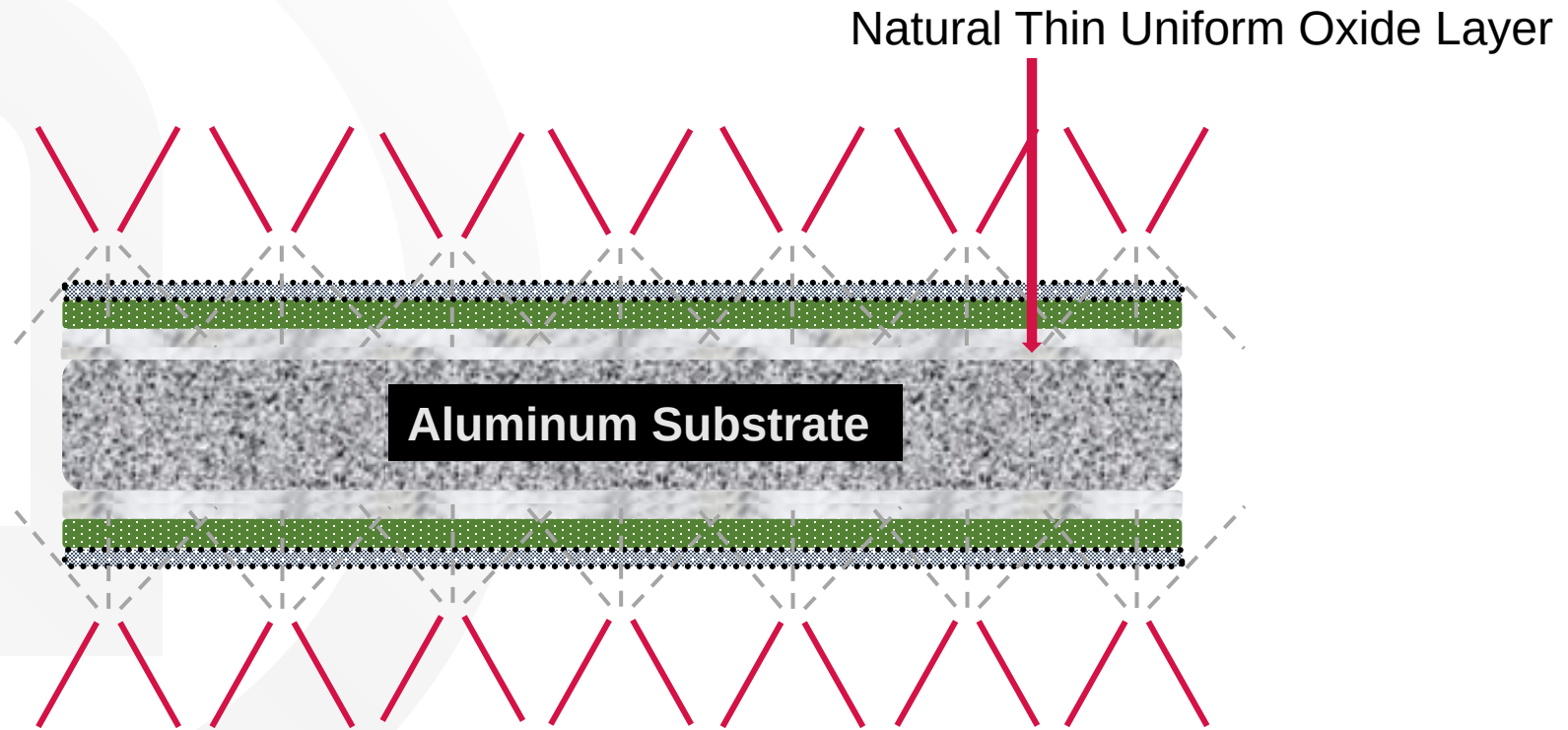
Repair of Aluminum Panels and BIW Parts

Controlled Natural Surface Oxide Formation for Bonding and Joining



- Aim is to stabilize the aluminium surface resulting in a better product performance:
 - Adhesive bond strength durability (prerequisite criteria)
 - Better spot welding performance (process, electrode life, weld quality)
 - Improved storage performance (in combination with pre-lubes)

Surface Deoxidation



Surface Degreasing and Deox Processes

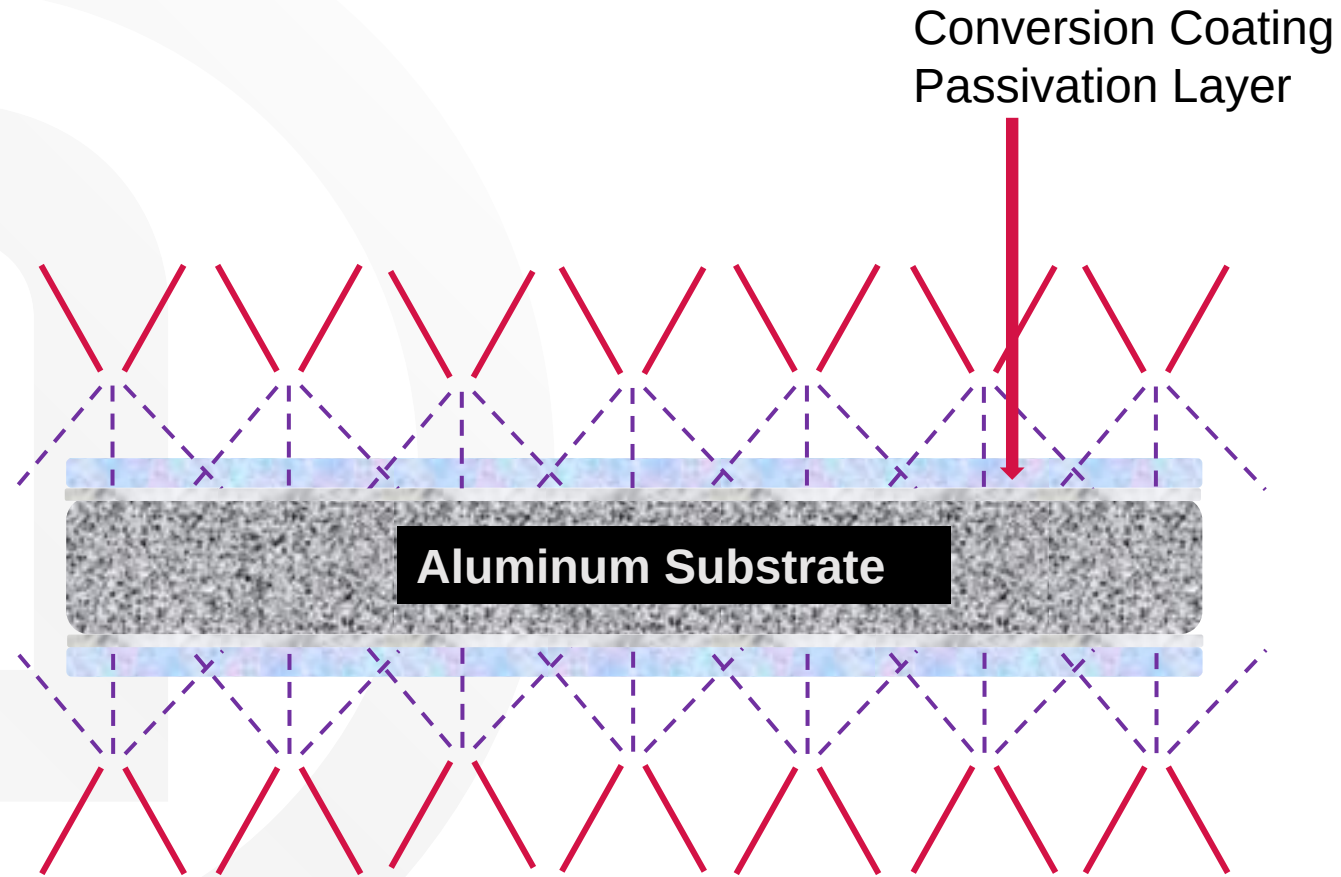


Degreasing

Pickling

Image Source: Andritz

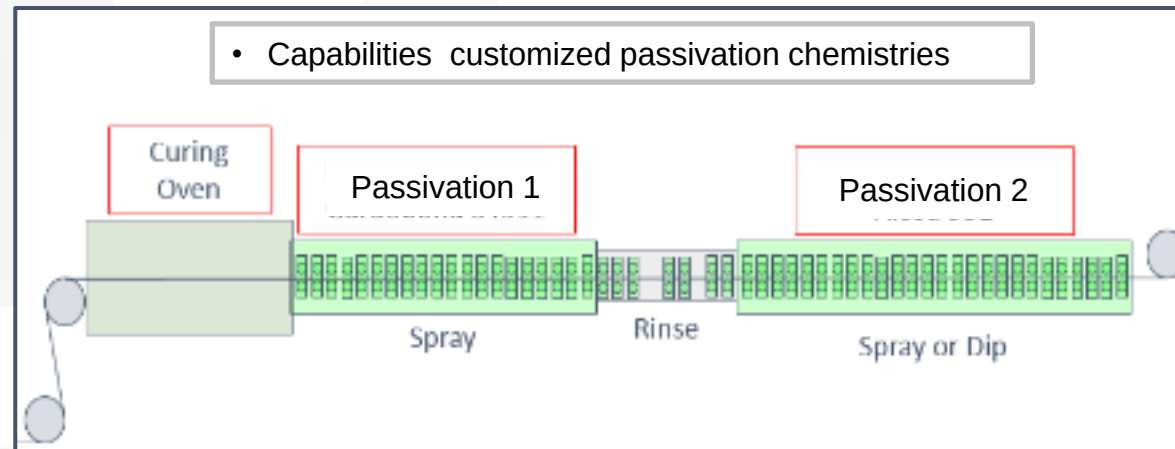
Surface Passivation



Pretreatment Process



Image Source: Andritz



- These chemical processes allow adhesive bonding, welding, and paint adhesion at the customer
- Both chemical sections utilize rinsing and drying of the sheet as it exits these sections

Outline

Understanding Corrosion

Surface Oxidation in Aluminum

Surface Coating Technologies

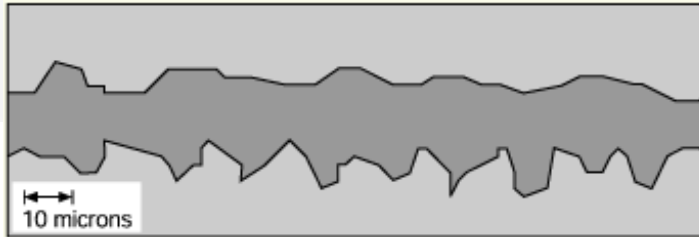
Adhesive Bonding

Repair of Aluminum Panels and BIW Parts

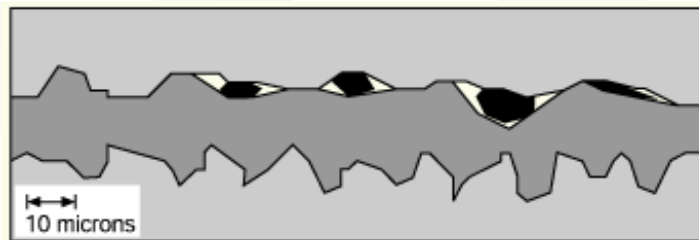
Accelerated VDA Corrosion Exposure



Example of adhesive joint

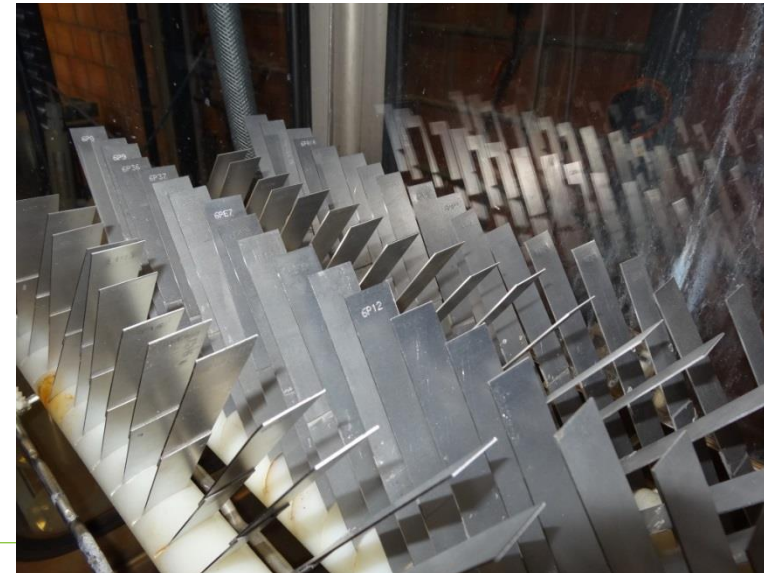


Cross-section of an adhesive joint with uniform surface



Cross-section of an adhesive joint with non-uniform oxides

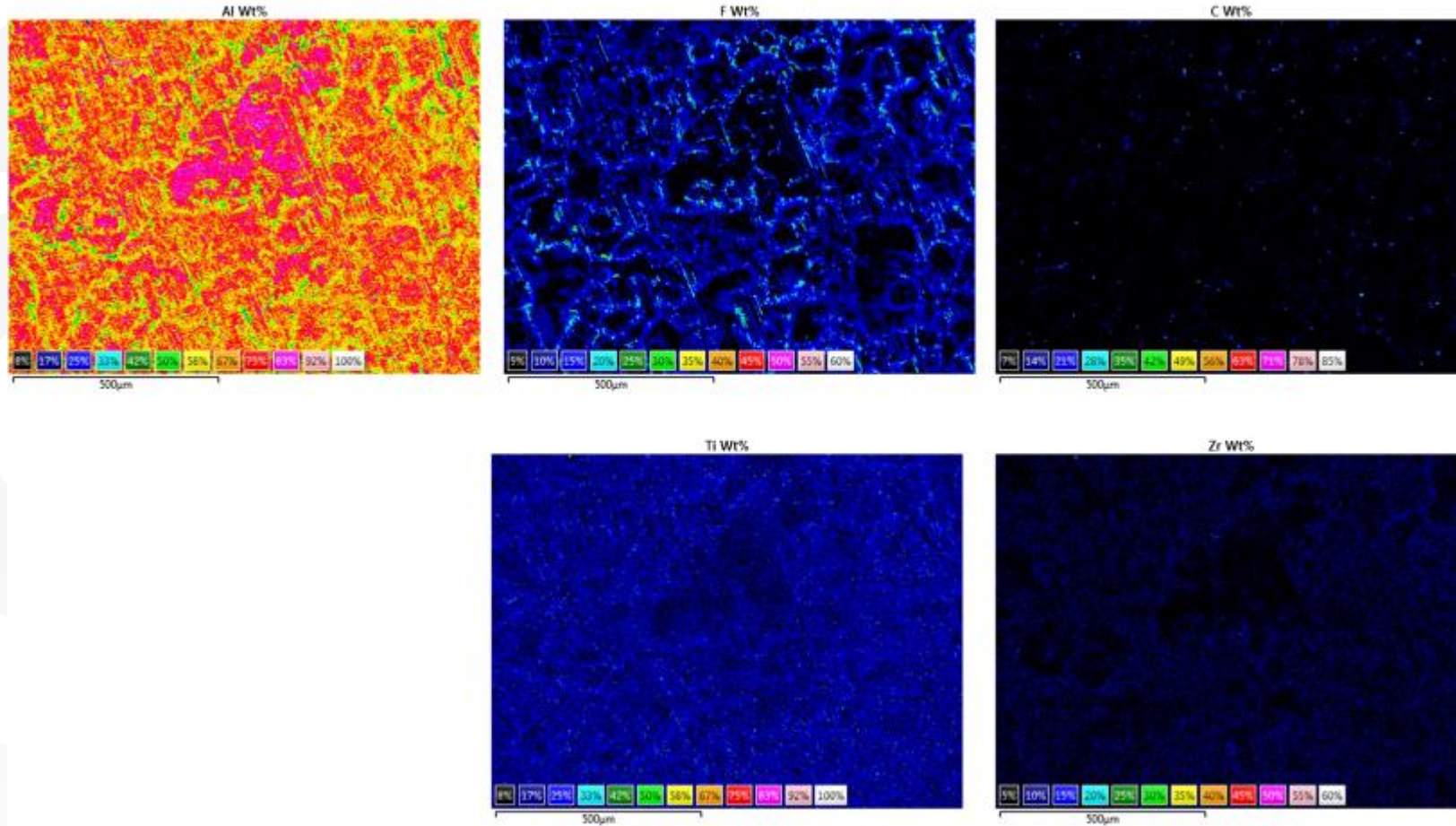
Source: Design Guide for Bonding Metals, Henkel 2011



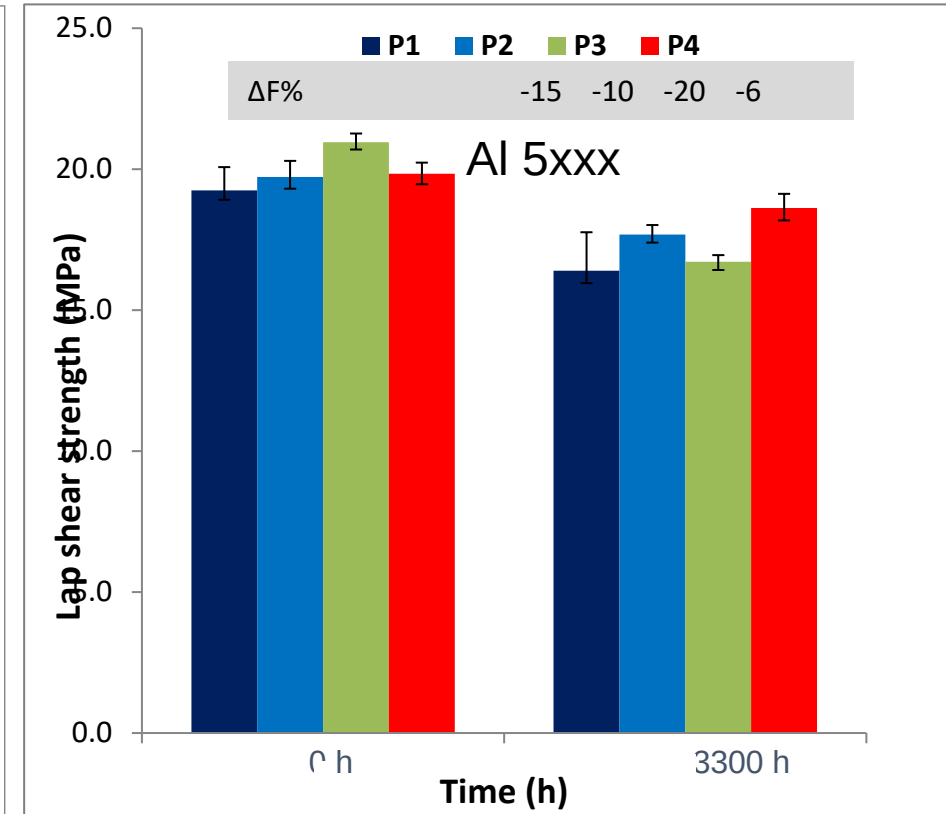
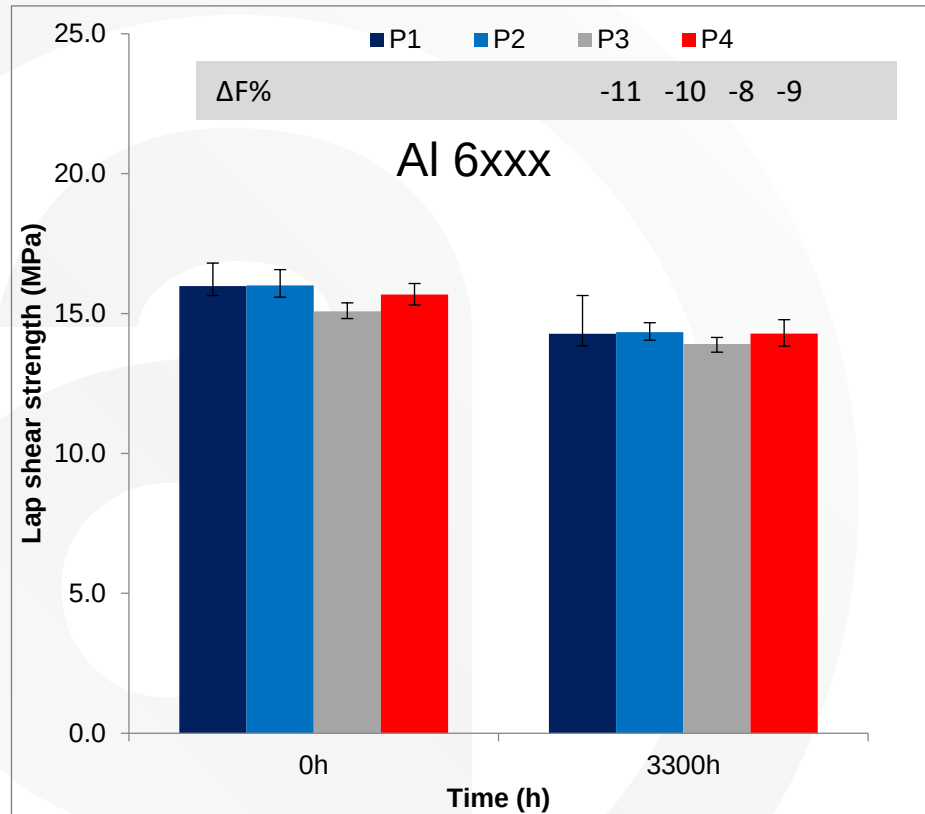
Samples exposed to VDA 621-415

Pretreatment Coverage

Analysis by FEG-SEM

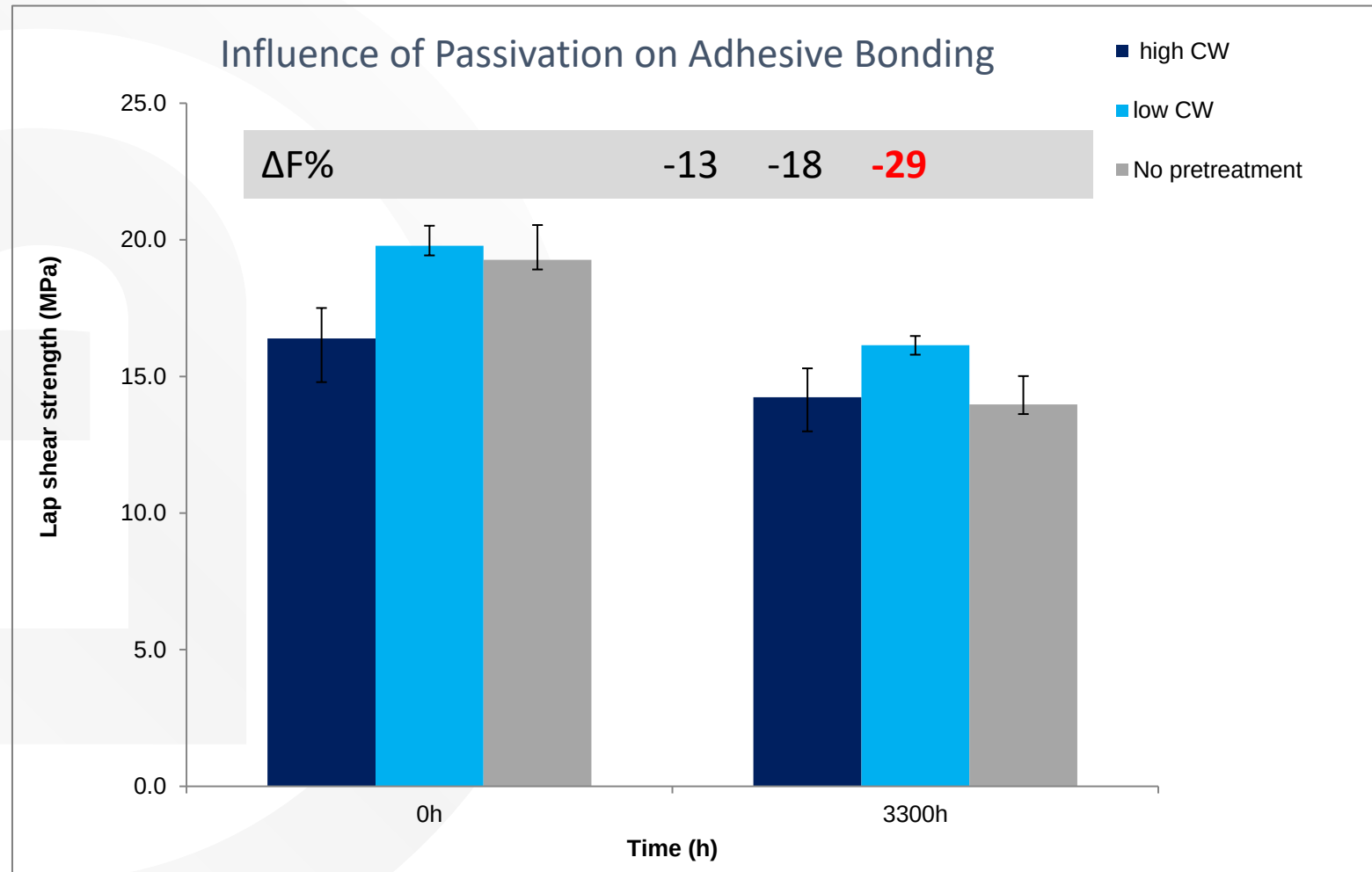


Pretreatment Evaluations on 5xxx and 6xxx Alloys



All pretreatments performances are comparable on 6xxx alloys but more distinctive on 5xxx alloys

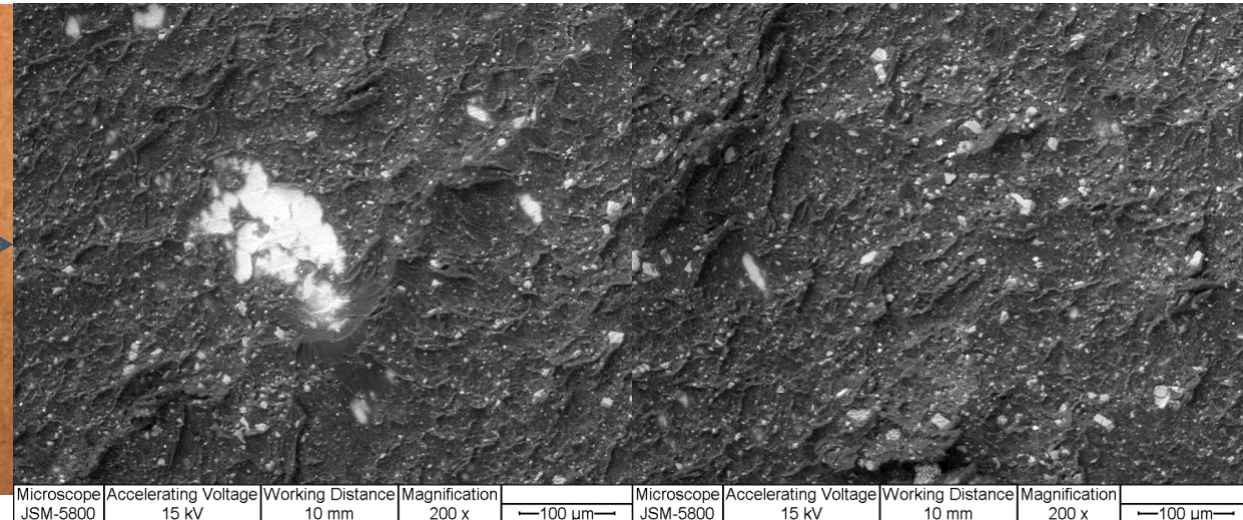
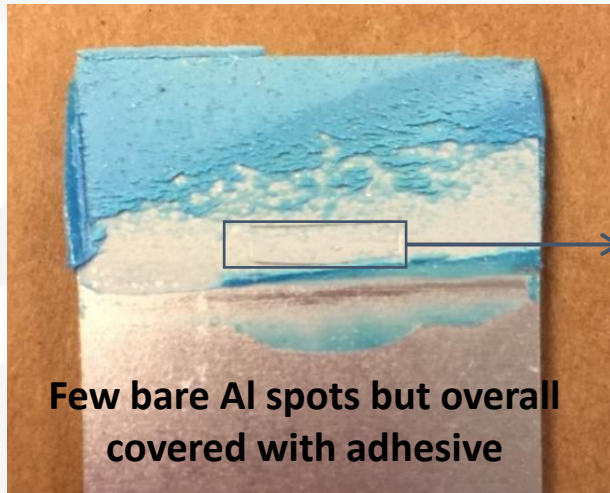
Pretreatment Coating Weights on 6xxx Alloys



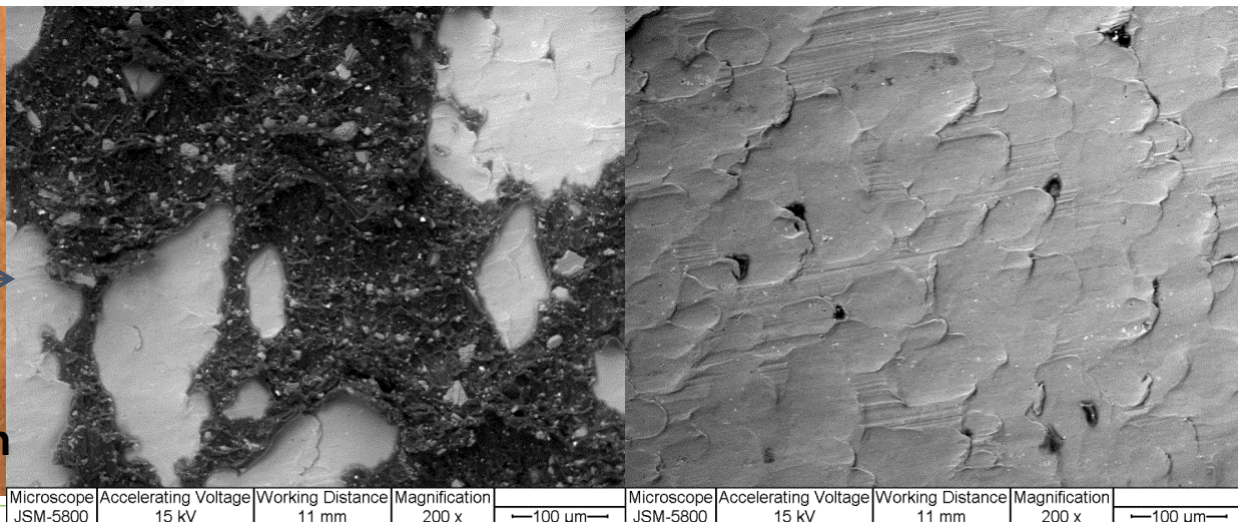
Passivation coating improves adhesive strength

SEM Analysis – High Coating Weight Passivation

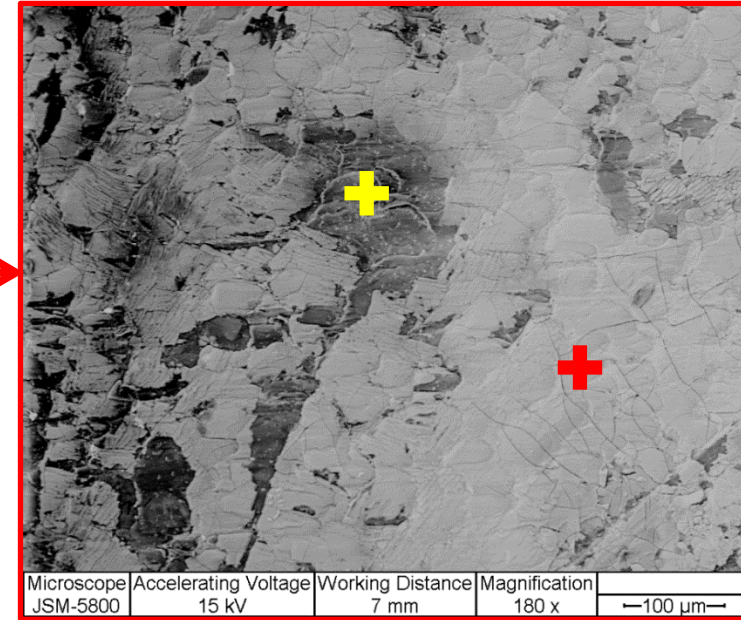
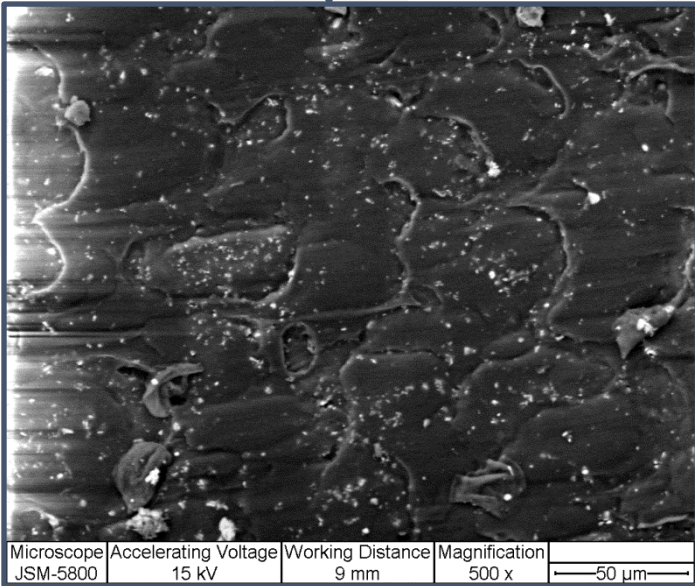
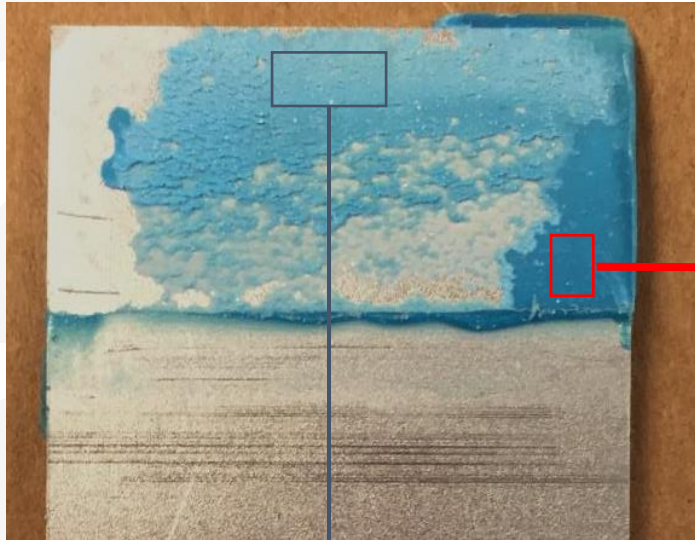
As produced
lap shear
coupons



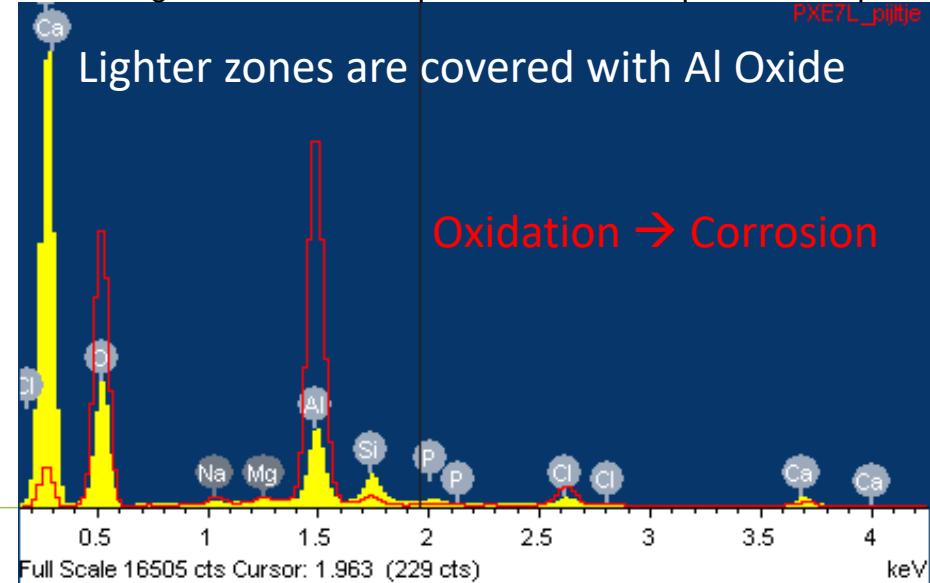
After 1500h VDA test



SEM Analysis – No Pretreatment



SEM Image of the corroded paired bonded coupon of the lap shear test



Summary

- Al has excellent corrosion resistance due to the thin (1-10nm) protective oxide film formation
- Reviewed types of corrosion and their mitigations
- Aluminum oxide is managed in order to achieve strength and durability for its intended characteristics
- Aluminum alloys **react** uniquely; proper surface oxide control is **critical**
- Pretreatment improves adhesive bond durability
- Pretreatment **coating weight** has a critical impact on **adhesive bonding** durability performance and **corrosion**

Outline

Understanding Corrosion

Surface Oxidation in Aluminum

Surface Coating Technologies

Adhesive Bonding

Repair of Aluminum Panels and BIW Parts

Repair of Aluminum Panels and BIW Parts

Not difficult, but different

- There are 30,000 repair shops in the US and 1/3 are certified for aluminum repair. Currently, there is more aluminum repair capacity than is needed.
- In US, about 70% of repair volume is “remove and replace.”
- Normally closure panels are easily replaced. For example, damaged hoods are unbolted and replaced rather than repaired.
- Aluminum panels are finished in the same way as steel panels including body fillers.
- All the major paint suppliers offer paint/primer systems for aluminum repair.
- All OEM with aluminum content have those procedures included in their repair manuals.

Repair of Aluminum Panels and BIW Parts

Not difficult, but different

- I CAR has worked with the aluminum industry to develop training guides for proper repair of aluminum and offered a nationwide training program since 1996.
- Tools for aluminum repair are generally similar to those used for steel repair. Good practice dictates that separate tools be maintained for steel and aluminum repair.
- Grinding wheels, files and sanding discs typically cut and remove aluminum easier than steel. Separate abrasives are used for steel and aluminum.
- Heat straightening – local heating can be used to straighten parts. However, aluminum does not change color when heated, so it is important to use temperature indicators to track temperature. Aluminum melts at roughly 1200°F, so care must be used when heating.

Repair of Aluminum Panels and BIW Parts – Joining Methods

Not difficult, but different

- Most aluminum assemblies use adhesives, heat can be used to separate bonded parts.
- Adhesively bonded joints can be repaired using a suitable surface treatment and common shop adhesive application.
- Battery powered self piercing rivet guns are used for repair riveting in many applications. A wide range of coated steel and aluminum drilled rivets are available for other repairs.
- Repair shops use conventional spot weld cutters and hole saws to remove spot welds and self piercing rivets.

A large, light gray stylized letter 'a' is centered on the left side of the slide. It consists of a thick circular outer ring and a thick, curved inner stroke that forms the letter 'a'.

Questions?