EUROPEAN ADHESIVE ENGINEER

MODULE 4.4

ELECTROCHEMICAL AND CORROSION EFFECTS ON ADHESIVE JOINTS

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4.4 Electrochemical and Corrosion Effects on Adhesive Joints

Scope:

- ✓ Exposure in electrochemically inert conditions
- ✓ Effect of high cathodic potentials
- ✓ Effect of impressed currents
- ✓ Effect of dissimilar metals in contact
- ✓ Effect of mechanical strain
- ✓ Effect of corrosion and adhesive joint failure

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4.4 Electrochemical and Corrosion Effects on Adhesive Joints

Scope:

- ✓ Theoretical models and failure mechanisms
- ✓ Increasing resistance to cathodic bond failure in adhesive joint applications

Exposure in electrochemically inert conditions [1]

Electrochemically inert system mean, that adhesive boneded joint is without any presence of electrical pair due to the presence of contact potential.

If bonded joint is adhesively bonded with a proprtietary adhesive/primer formulation, in electrochemically inert conditions these joints will be very stable and show no significant loss in strength even after three years immersion in seawater.

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Effect of high cathodic potential [2]

High cathodic potential may emanate from the electrolytic cell that exists at the surface of a corroding metal. Water, oxygen and some liqiud electrolites are required to establish a electrolytic cell ad adhesive/adherend interface. Localized damage of the adhesive leads to the exposed metal surface. In the case of steel, it undergoes through the anodic reaction, which will eventually lead to a characteristic rust deposit on the surface:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The electrons produced by this reaction are consumed in the cathodic reaction, which occurs adjacent to the anodic area, and may involve both oxygen and water:

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Effect of high cathodic potential [2]

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$$

The cathodic reduction of water and oxygen leads to the production of hydroxyl ions, which in turn leads to an increase in the pH of the electrolyte in the environs of the adhesive/adherend interface.

This alkalinity is responsible for the rapid failure of adhesive joints and has given rise to the term cathodic disbonding. The cathodic reaction will occur at any regions of exposed metal, bringing about rapid failure of the adhesive joint.

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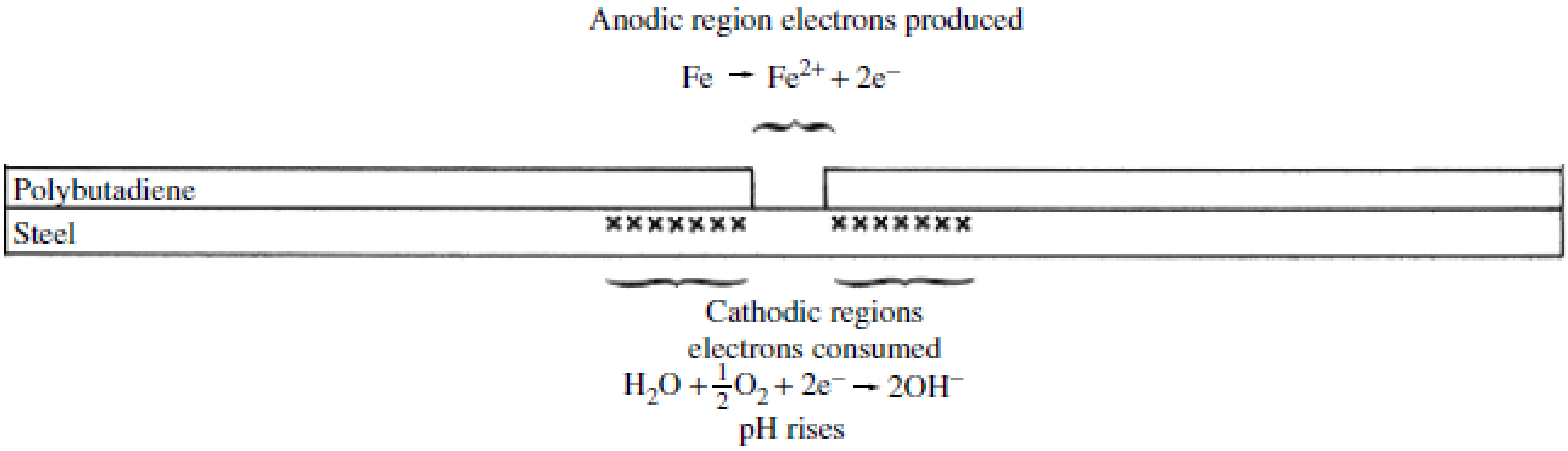
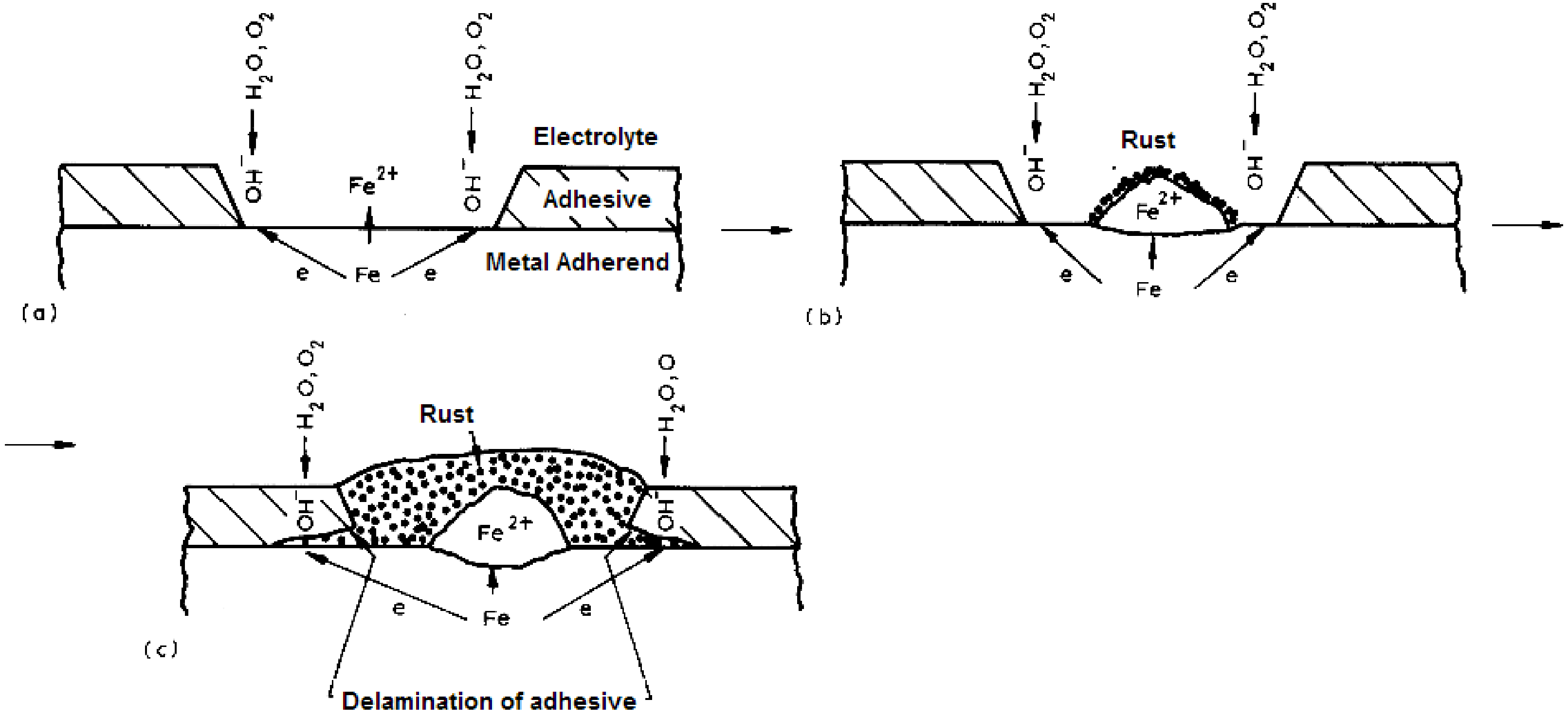
Effect of high cathodic potential [3]



Electrochemical reactions involved in cathodic disbonding in a system at rest potential (polybutadiene on steel exposed to 0.5 M NaCl)

Effect of high cathodic potential [2]



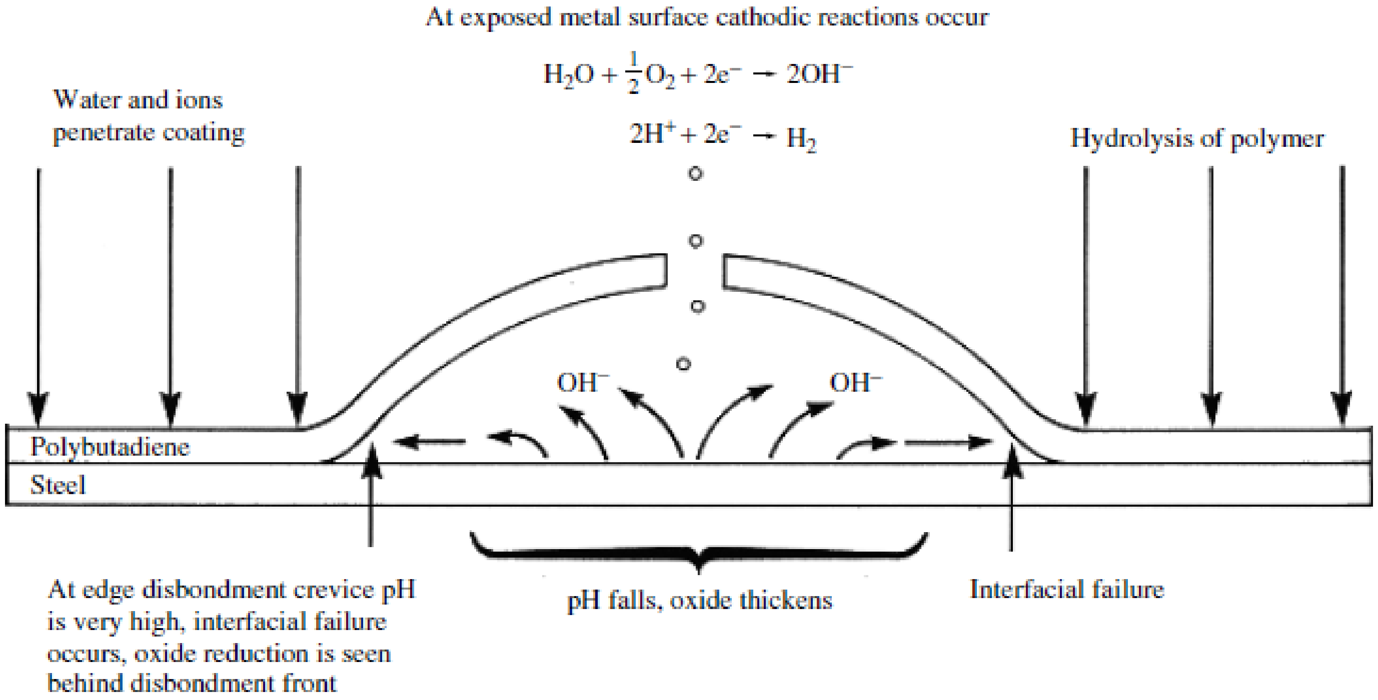
Mechanism of cathodic disbonding at adhesive/adherend interface

Effect of impressed current [3]

Joints made with steel and other metals can also be subject to cathodic disbonding if they are immersed in an electrolyte and subjected to a cathodic potential, such as that created when the adherend is in electrical contact with a more electrochemically active metal.

Impressed current to the adhesive joint can be regarded as cathodic protection. This process is frequently used to prevent corrosion of massive steel structures as ships or pipelines. Corrosion of the adherend is suppressed by this process.

Effect of impressed current [3]



Electrochemical reactions involved in cathodic disbonding in a system that is cathodically protected by an impressed current -1,5 V (polybutadiene on steel exposed to 0.5 M NaCl)

Effect of dissimilar metals in contact [1], [5]

Adhesives can prevent electrochemical corrosion in joints between dissimilar metals. Particular problem is adhesive bonding of clad aluminium alloys (ALCLAD). With clad aluminium alloys the electrode potential of the clad layer (usualy from thin layer of technical pure aluminium) is generaly higher than the base aluminium alloy. Clad metal is anodic with respect to the base alloy. In a corrosive envirnment the cladding layer will be consumed, thus protecting tha base metal.

This mechanism of corrosion inhibition can be effective for exposed aluminium structures. In context of adhesive bonding the clad layer is undesirable. Once clad layer has dissapeared the joint strength will not be very high.

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Effect of dissimilar metals in contact [1]

Galvanic cell may be established between cladding and underlying alloy with the progressive destruction of the interfacial region. Attachment of the adhesive to metal layer which is anodic with a respect to the rest of metallic system is always undesirable in terms of corrosion resistance.

Chemical components in the adhesive may diffuse into the electrolyte. If the adhesive is an amine-cured epoxy any unreacted amine diffusing into the region of corrosion could affect the local pH of the electrolyte.

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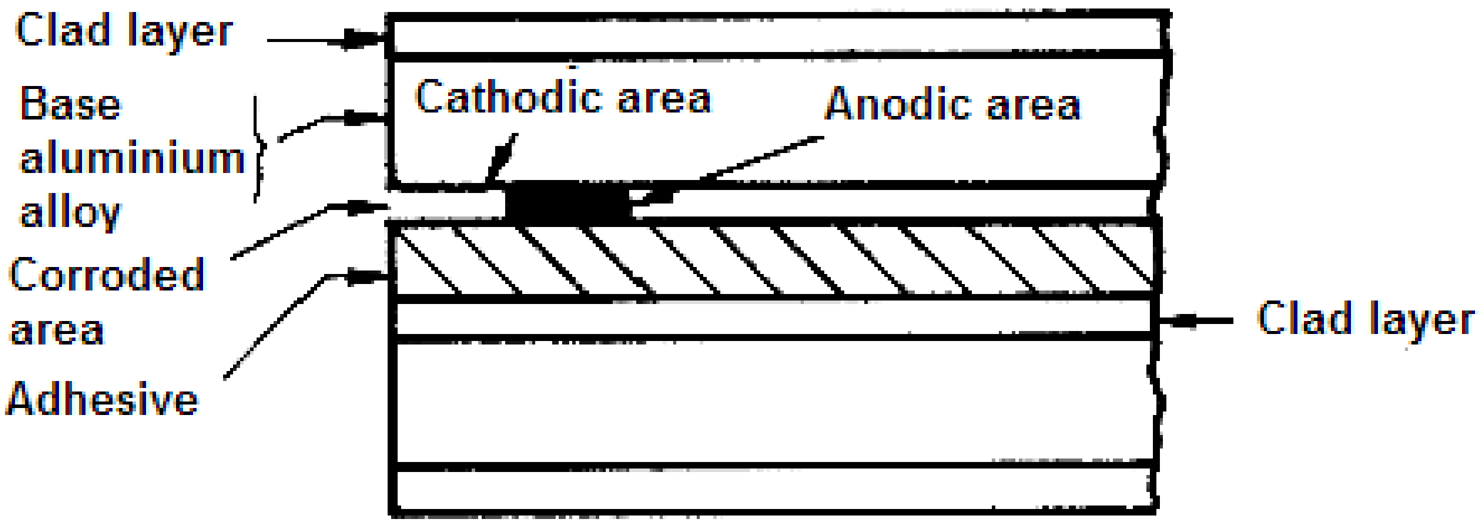
Effect of dissimilar metals in contact [1]



Corrosion as a primary mechanism of environmental attack on clad aluminium alloy joints

Effect of dissimilar metals in contact [4]

Example: Adhesive-bonded joints between a 0.8 mm thick cold-rolled (CR) steel sheet of 270 MPa tensile strength and a 1.2 mm thick aluminum alloy sheet (AW-5182/AW-6022) for automotive body:

- Used one component heat curing structural epoxy adhesive
- Curing in a atmospheric furnace at +170°C for 20 minutes
- Testing speed in shear strength testing 50 mm/min
- Application for joining dissimilar metals in automotive industry

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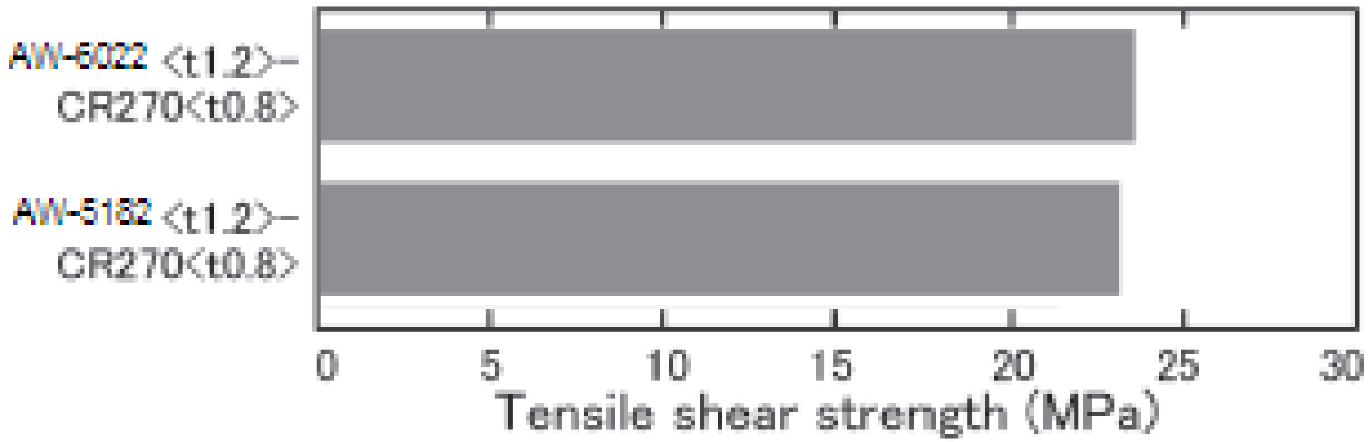
Effect of dissimilar metals in contact [4]



Joint strength exceeding 20 MPa

Mode of failure is always cohesive

Failure occurs in the adhesive

Tensile shear strength of adhesive joints for steel and aluminum alloy sheets combination

Effect of corrosion and adhesive joint failure [1]

Another mechanism of attack upon adhesive joints by moisture, which may lead to loss of joint strength and greatly reduce the service life , is relatively gross corrosion of adherends. Signs of gross corrosion are observed on the fracture surfaces of joints, which have suffered environmental attack.

Such corrosion may have frequently resulted after failure has occured in the interfacial regions of the adhesive bonded joint. Corrosion of the adherends is a post-failure event, rather than a prime cause of environmental failure.

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Effect of corrosion and adhesive joint failure [1]

Adhesive bond failures of aluminium alloy joints unter moist corrosive service conditions are due to corrosion of the aluminium surface in the interfacial area.

Corrosion must be considered as an after effect rather than the primary cause of bond failure. There exists relationship between the mechanism of corrosion and cathodic bond failure.

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Effect of corrosion and adhesive joint failure [5]

Role of corrosion in the failure of adhesive joints:

- The behavior at cathodic and anodic areas is very different
- At the cathodic areas the reduction of water and oxygen leads to the production of hydroxide ions and the generation of a higher pH locally.
- If gross corrosion occurs beneath the adhesive, failure will occur in the corrosion product itself which is the result of the anodic half reaction and the failure surfaces will be decorated with anions such as chloride.

Theoretical models and failure mechanisms [6]

Failure mechanisms of adhesive joints on aluminium alloys due to corrosion on the adhesive side:

- microcracks that causing failure close to the interface in weak boundary layers
- stress hydrolysis of primary covalent bonds due to humidity
- water desorbing the adhesive due to greater affinity for the aluminium surface through the formation of hydrogen bonds

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Theoretical models and failure mechanisms [6]

Failure mechanisms of adhesive joints on aluminium alloys due to corrosion on the adherend side:

- structural transformation in aluminium oxide
- significant differences between the wettability potential on aluminium oxide
- cathodic or anodic activity at the adherend (cathodic disbonding or anodic undermining)

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Increasing resistance to cathodic bond failure [7]

Cathodic disbonding

Cathodic disbonding is the loss of adhesion between adhesive and adherend due to the products of cathodic reduction reaction (corrosion reaction) that take place in the interface of adhesive bond.

Disbonding of adhesive joint occurs when adhesive in a cathodic protection system interact either chemically or physically, ultimately causing corrosion beneath the adhesive.

Increasing resistance to cathodic bond failure [7]

Adhesive joints not uncommonly fail in an aqueous environment. One of the mechanisms by which this may occur on metals is by cathodic disbonding.

Cathodic disbonding (or delamination) occurs when failure of an adhesive joint is associated with a cathodic potential on the metal adherend, a phenomenon most widely considered with respect to iron-based alloys.

Increasing resistance to cathodic bond failure [7]

Electrochemical potential has the most dominant effect on cathodic disboding failure rates. For a given electrolyte, cathodic disvbonding was found to depend on:

- cathodic voltage (or current density),
- temperature,
- applied strain energy release rate.

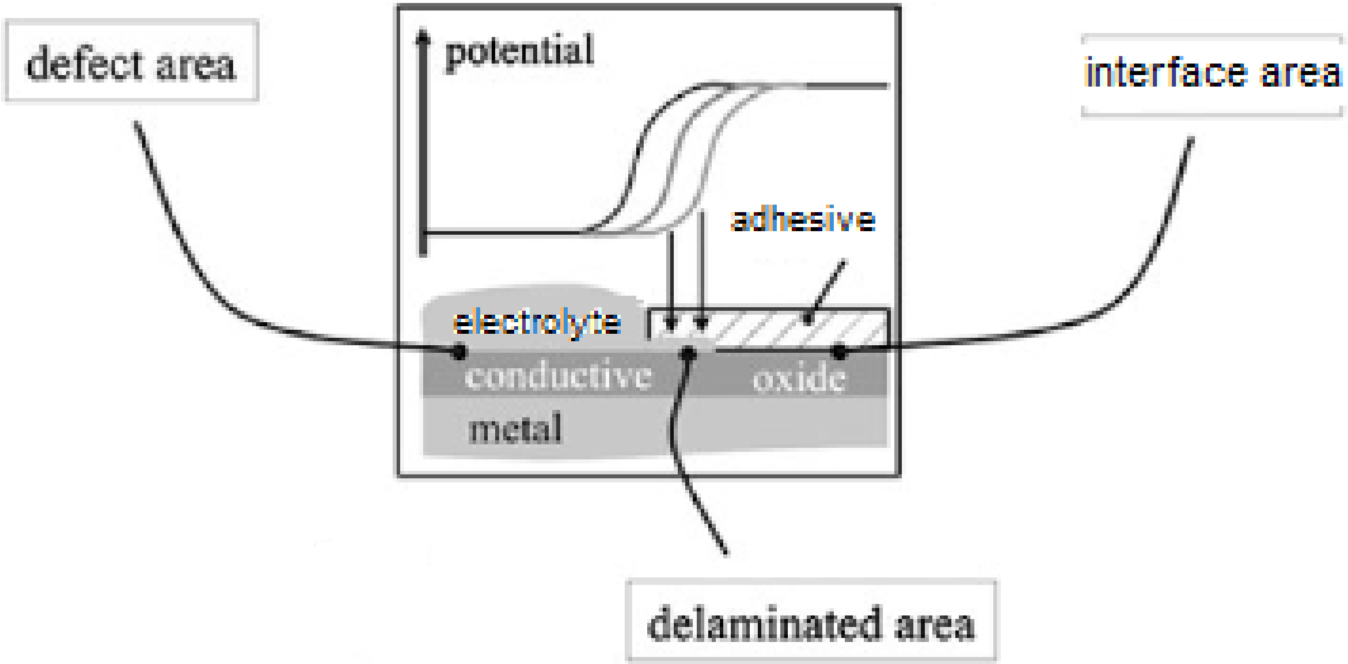
Increasing resistance to cathodic bond failure [7]

Prior to cathodic disbonding, two separated galvanic cells are active in the adhesive joint:

- metal dissolution
- oxygen reduction

Oxygen reduction at the intact epoxy/adhesive substrate is inhibited, because metal dissolution is supressed and only oxide oxidation occurs. This leads to more anodic potential at steady state conditions of the galvanic cell. As soon as electrolyte penetrates the adhesive/oxide/adherend interface, a conductive connection between defect and adjecant adhesive is established. Oxygen reduction process is released and the interface potential is shifted down to the defect potential.

Increasing resistance to cathodic bond failure [7]



Cathodic disbonding process in metal/conductive oxide/adhesive system

Increasing resistance to cathodic bond failure [7]

Cathodic disbonding performance is much more consistent at thicknesses of adhesive over 200 µm. Therefore, thicknesses less than 200 µm should be avoided in order to achieve good cathodic disbonding protection.

Factors affecting disbonding, that are choice for increasing resistance to this phenomena:

- thickness of the adhesive layer
- chemical composition of the adhesive
- cure percentage

Increasing resistance to cathodic bond failure [7]

Epoxy adhesives with anti cathodic disbonding performace:

- bisphenol epoxy resin
- curing agent of polyamide and modified phenolic amine in the ratio 2:1

Cathodic disbonding inhibitors:

- must be a weak acid and a reducing agent simultaniously
- self condensated sterically hindered phenol resin

Resistance to corrosion of adhesive bonds in Al [7]

1.) The degradation in joint strength and failure mode are primarily attributed to the polar component of work of adhesion between adhesive and aluminium adherend which are being destroyed by corrosion of the latter in the overlap region of the bonded joints. This degrades both polar and dispersion components of work of adhesion between adhesive and aluminium adherend.

2.) The elevated temperature significantly accelerate the corrosion reaction of aluminium adherend, which speeds up the degradation in joint strength.

Bibliography

[1]	A.J. Kinloch: Adhesion and Adhesives-Science and Technology, Springer, 1987
[2]	D.E. Packham: Handbook of Adhesion, 2 nd. Ed. , John Wiley and Sons, 2005
[3]	A. Pizzi, K.L. Mittal, Ed.: Handbook of Adhesive Technology, Marcel Dekker, 2003
[4]	Dissimilar Metal Joining Technologies for Steel Sheet and Aluminium Alloy Sheet in Auto Body, Nippon Steel Technical Report No. 103, May 2013, 91-98
[5]	A. Öchsner, R. D. Adams, L. F. M. da Silva, Ed.: Handbook of Adhesion Technology, Springer, 2011
[6]	J.D. Minford: Handbook of Aluminum Bonding Technology and Data, CRC Press, 1993
[7]	L. F. M. da Silva, Chiaki Sato, Ed.: Design of Adhesive Joints Under Humid Conditions, Springer, 2013

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