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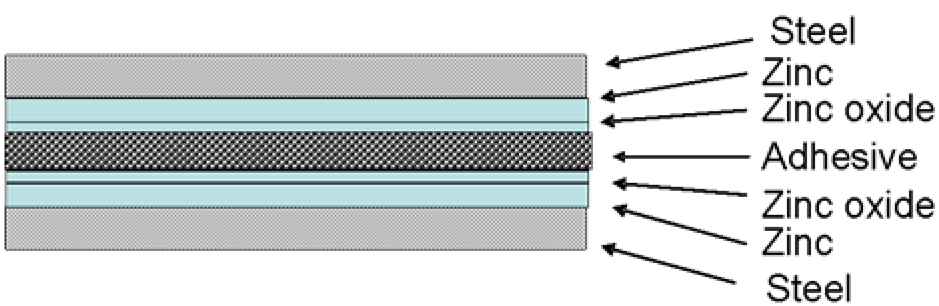
Understanding of the adhesion mechanism to zinc-coated steel

M2i Project nr: M22.06.09332



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Aim of the project

- Understand how surface chemistry relate to the adhesion strength and corrosion resistance of an adhesive joint for both galvanized steel (GI) and Magizinc (MZ) coated steel

How we can achieve this?

- Insight will be obtained by analysis of the chemical components and their interactions at the interface: - XPS, - FT-IR, - SEM/EDX, contact angle)

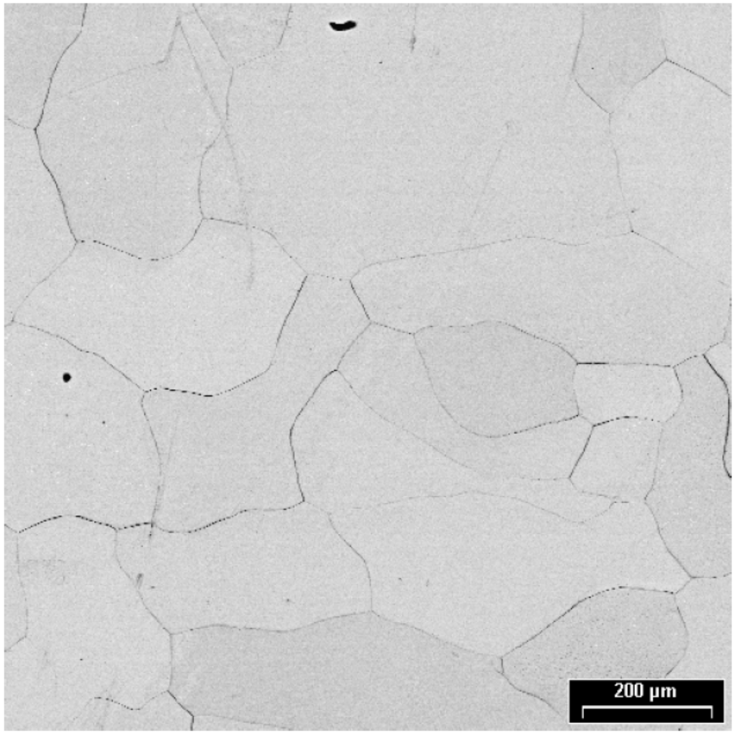
- Feedback from lap-shear tests (initial, and after salt spray)

- Translate results into actions in running production line at Tata steel

Surface Morphology

Galvanized steel (GI)

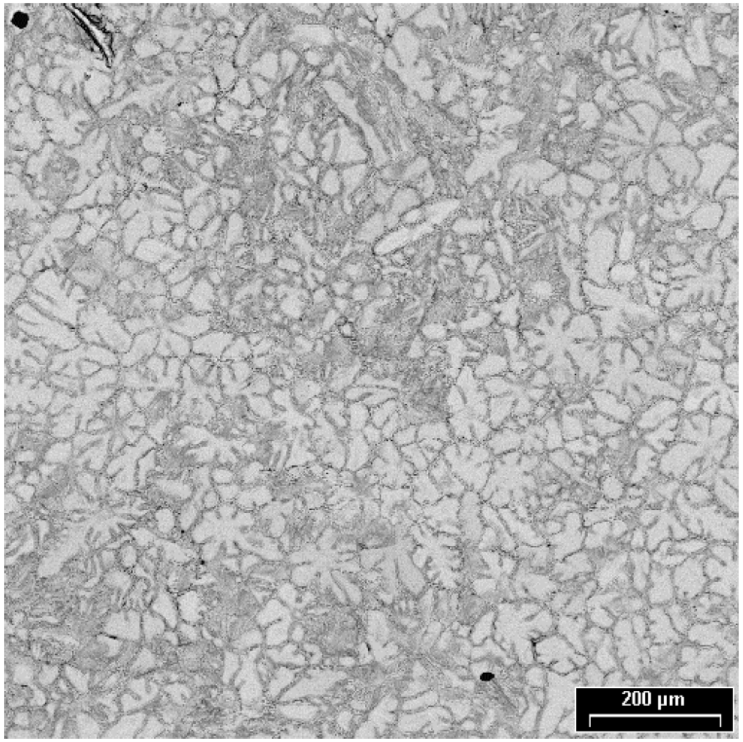
Zinc coating with 0.2%Al and no Mg



top view of GI

MagiZinc (MZ)

Zinc coating with 1.5%Al and 1.5 %Mg

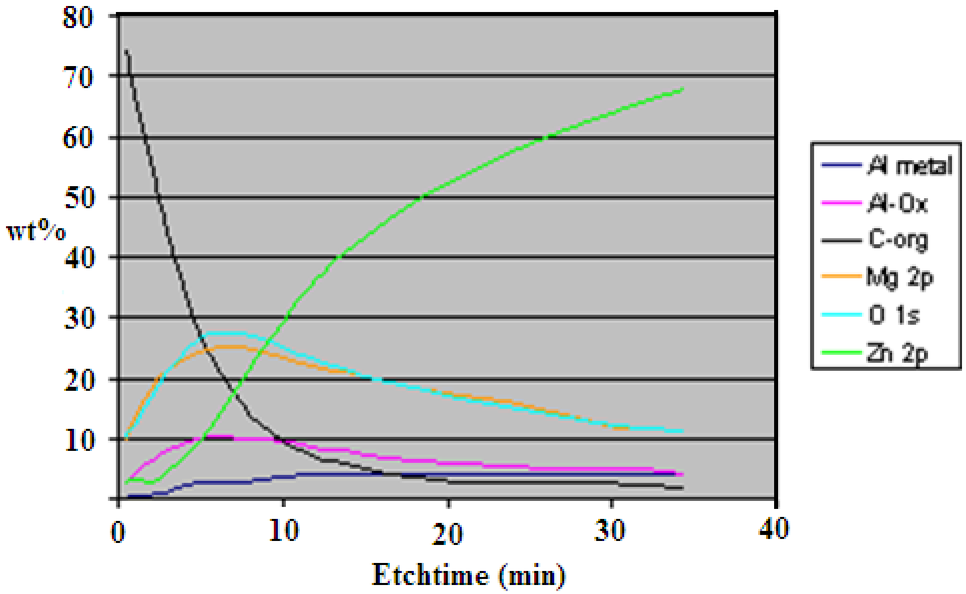


top view of MZ

Surface segregation of alloying elements

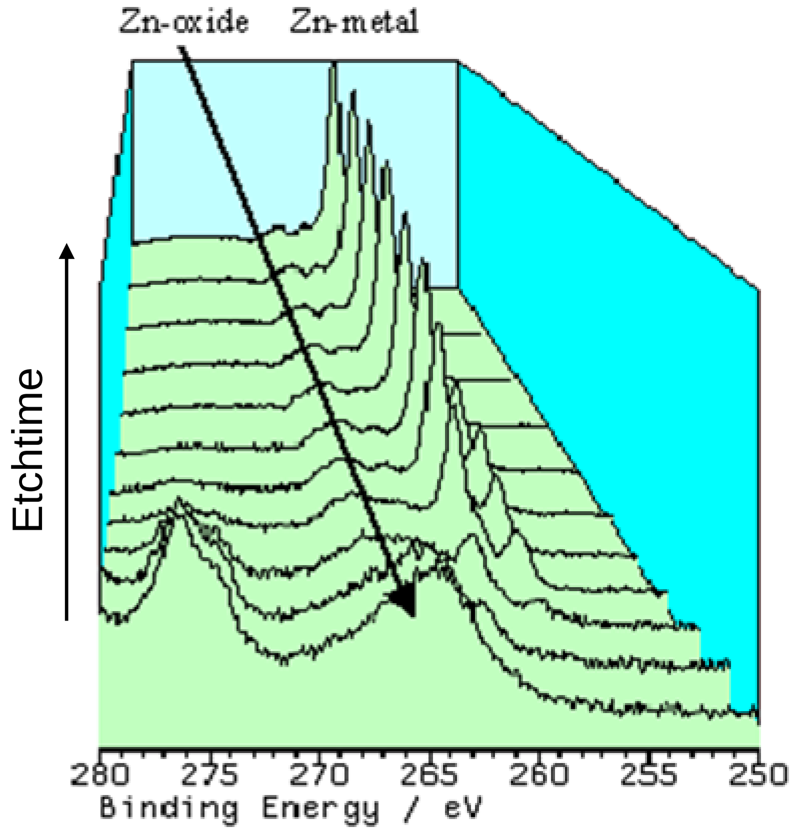
- Alloying elements are insoluble in the Zn matrix and segregate to the surface during cooling of the coating

XPS depth profile of a MZ surface



- Composition outer layer MZ: Zn:Al:Mg ~ 1:1:2 and GI: Zn:Al ~ 1:1

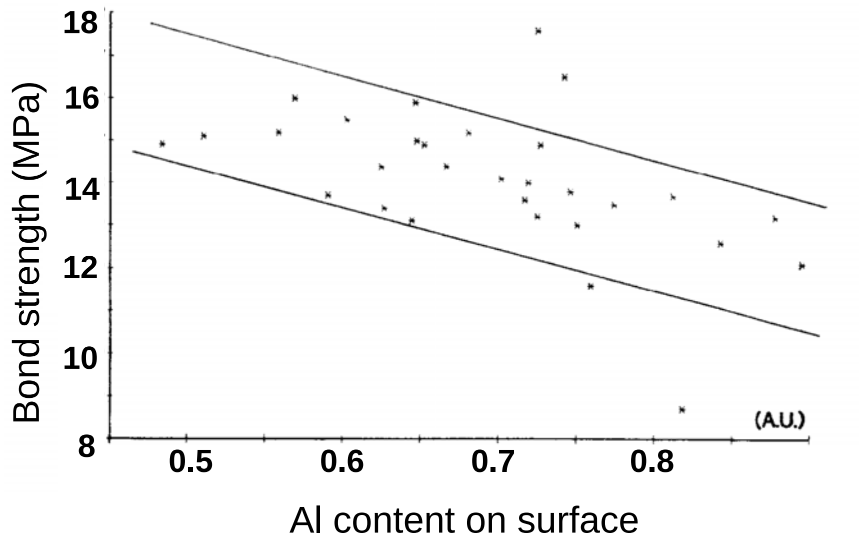
- Relatively large amount of carbon species remain on surface after degreasing



- High oxidation potential of Mg and Al causes hardly any metallic Mg and Al to be present at surface

- ZnO only present in high quantities at outermost surface

Influence surface chemistry on bond strength GI



- Aluminum is inactive and reduces bond strength

Single Lap Shear tests

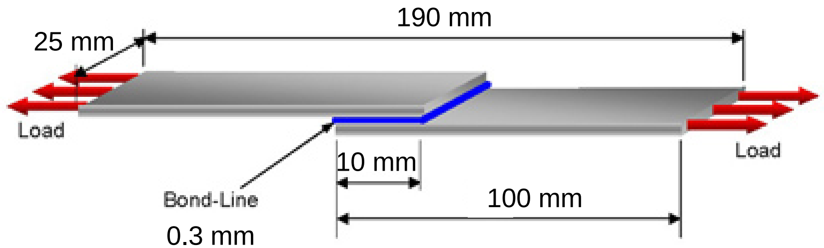
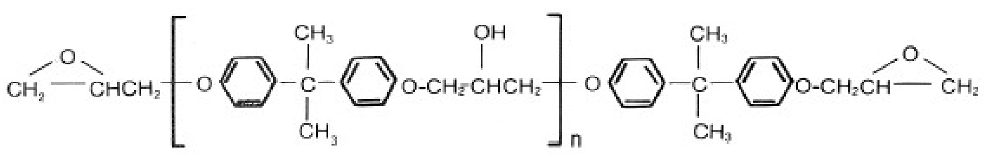
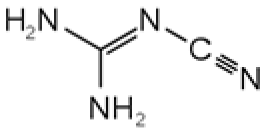


Illustration of lap shear joint

All specimen have been ultrasonically degreased in heptane

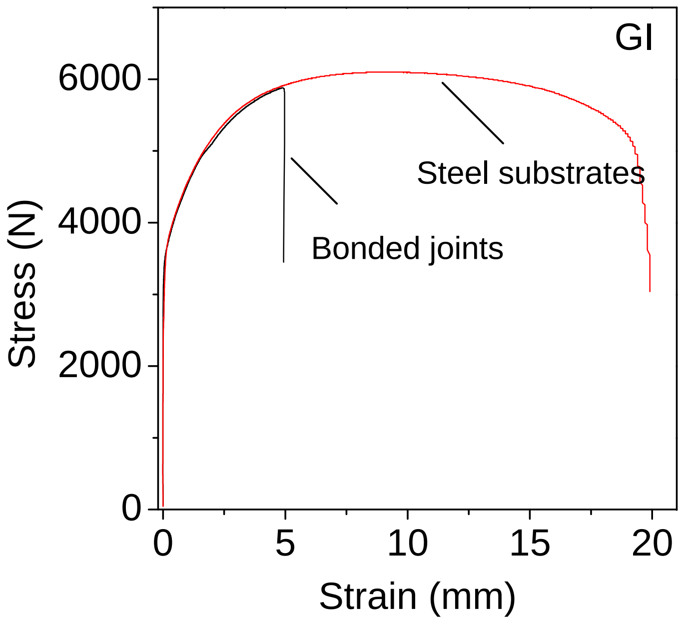
Applied adhesive: Dow Betamate^{TM} 1496 V (1-part epoxy adhesive) based on:

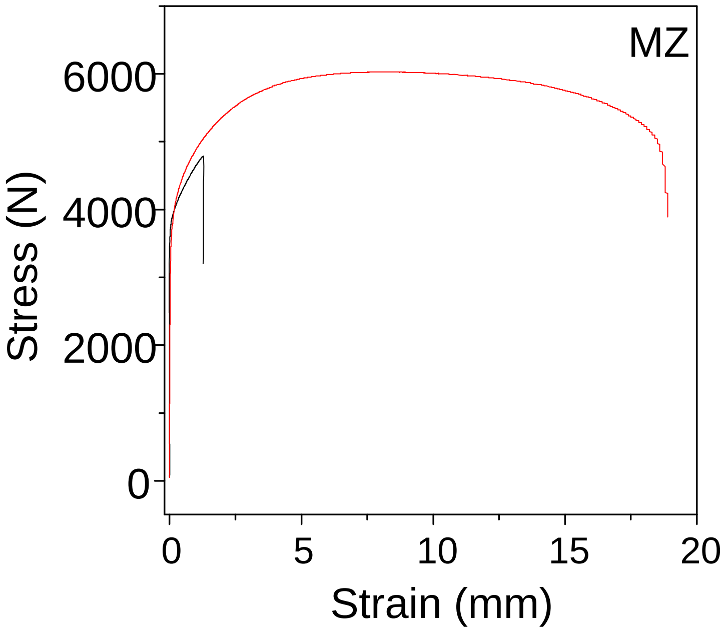




Dicglycidylether of bisphenol A and dicyandiamide (curing agent)

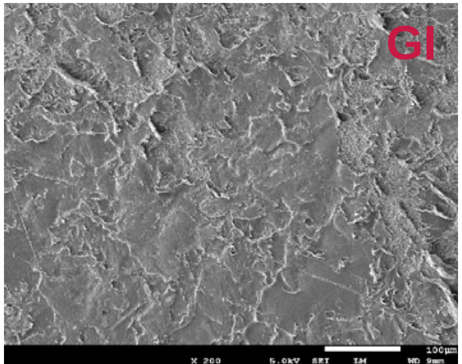
Stress-strain behavior GI and MZ for similar steel types

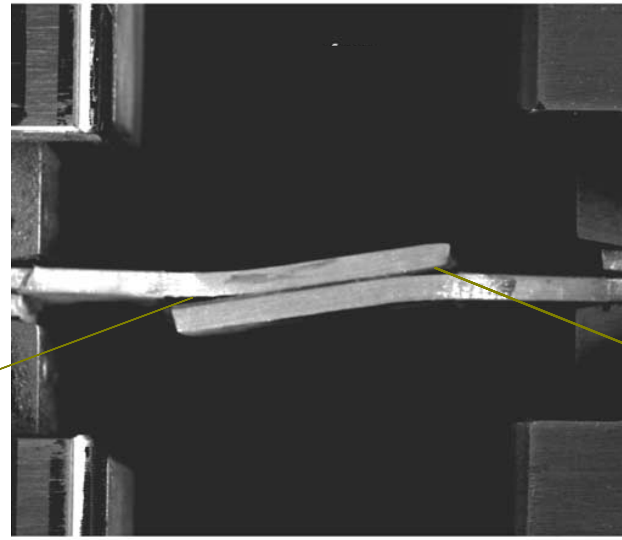


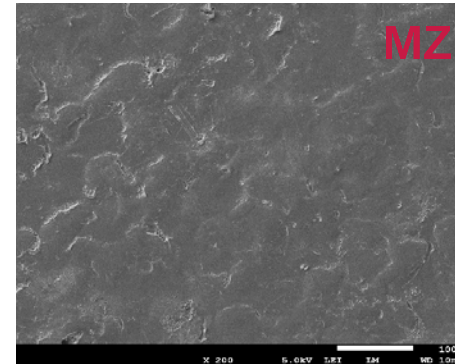


GI performs better than MZ

Single Lap Shear tests: Fractured Surfaces

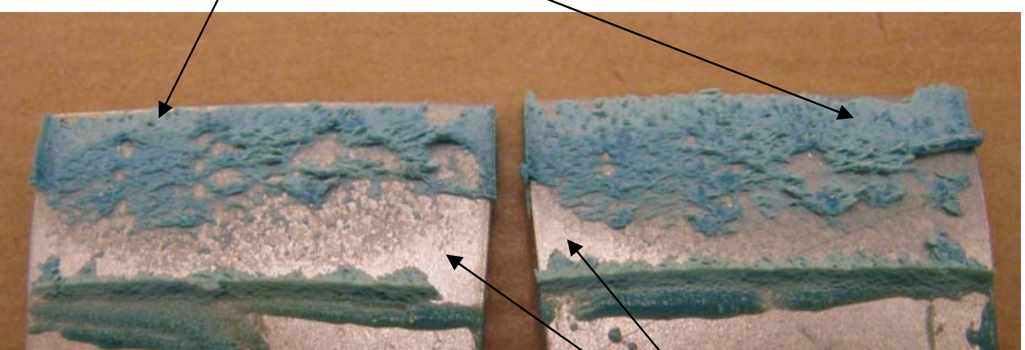


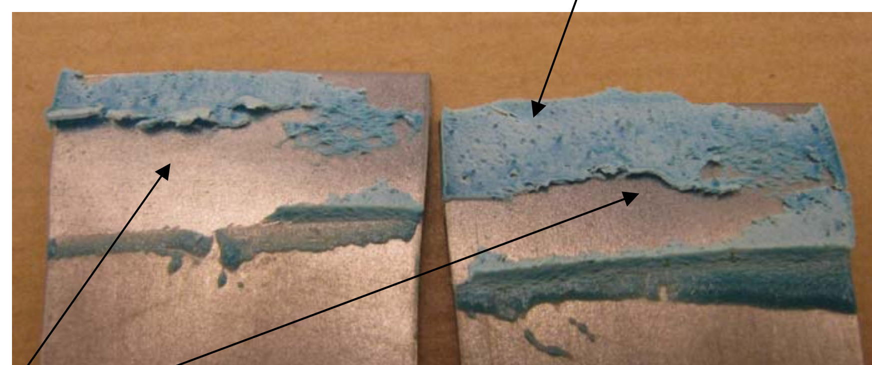




Peel zone

Peel zone



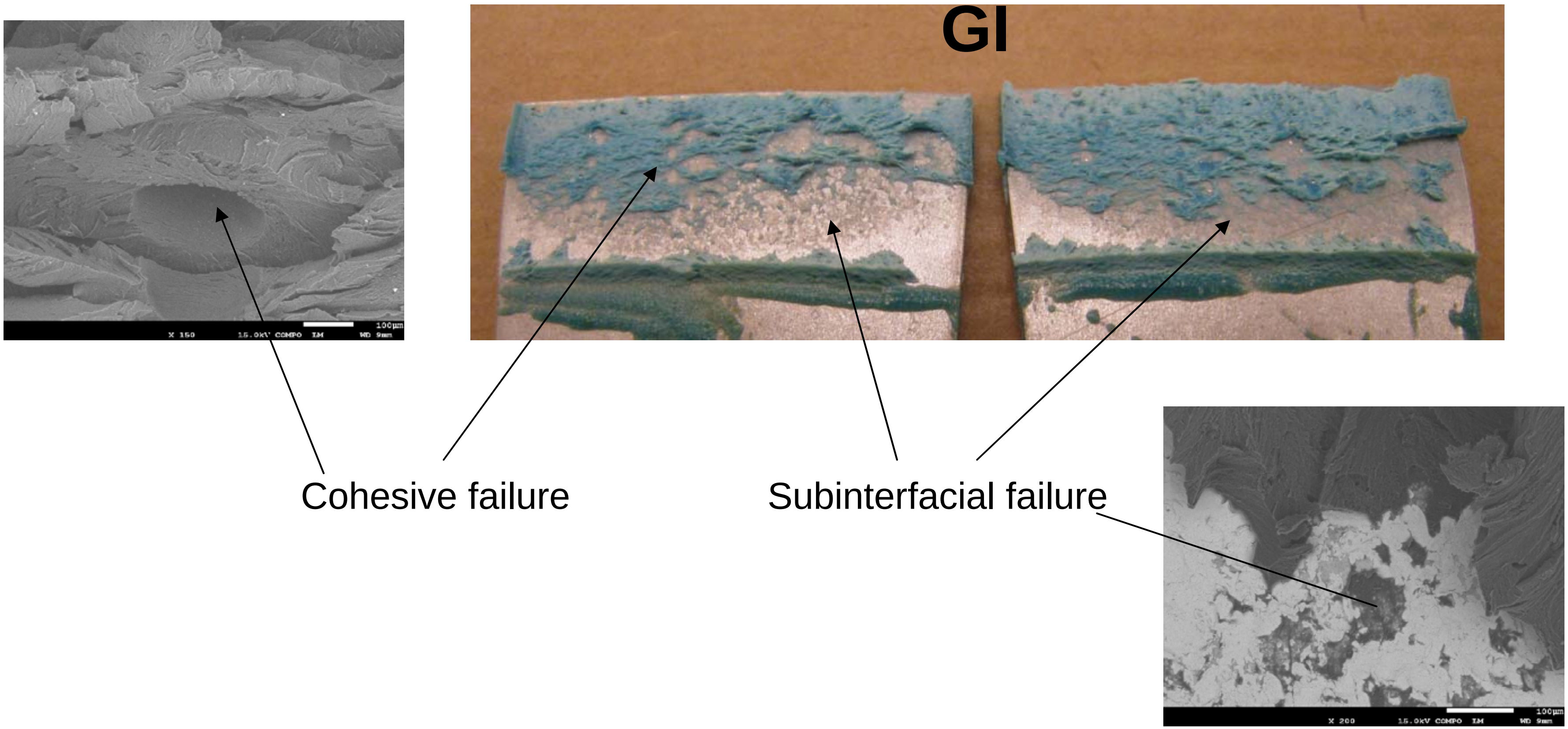


GI

Interfacial failure

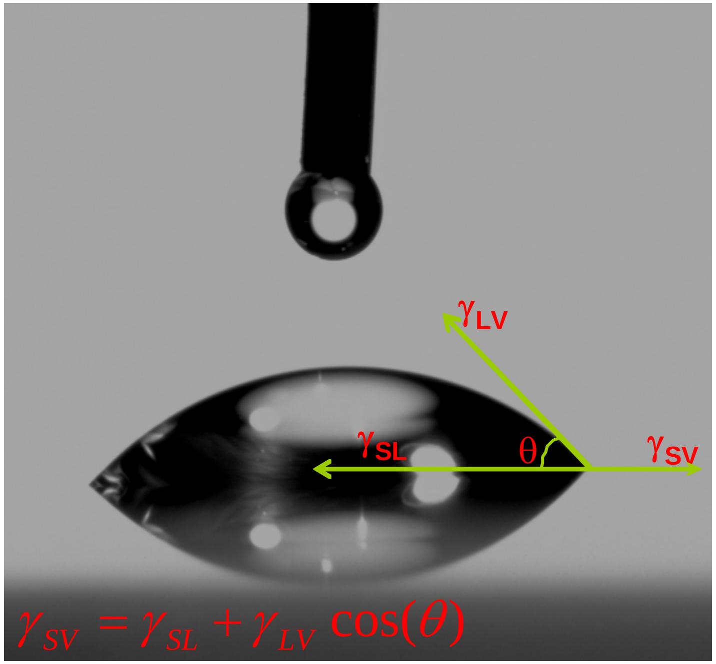
MZ

Single Lap Shear tests: Fractured Surfaces



Wetting and acid-base interactions determined by contact angle titrations

Surface energy (γ) components can be calculated by the method of Owens/Wendt:



separating the surface energy into a dispersive and polar component:

$$\gamma^{tot} = \gamma^{d} + \gamma^{p}$$

Owens-Wendt equation:

$$\gamma_{LV}(1+\cos\theta) = 2\left(\sqrt{\gamma_{LV}^{d}\gamma_{S}^{d}} + \sqrt{\gamma_{LV}^{p}\gamma_{S}^{p}}\right)$$

Acid-base components of surface energy are obtained with the method of Good/vanOss:

Separating the surface energy into a Lifshitz -van der Waals (LW) and Acid-base (AB) component:

γ+ γ-

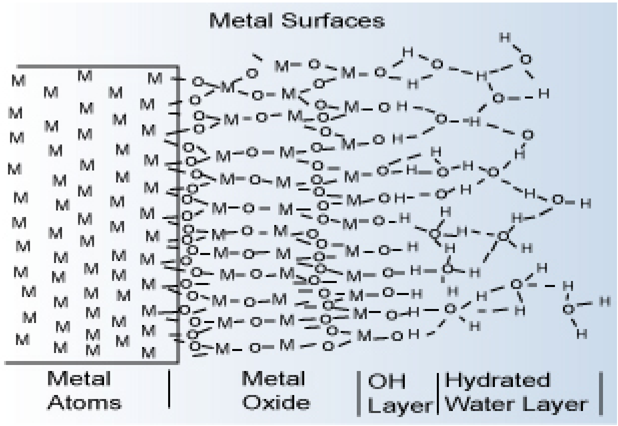
$$\left(\gamma_{S}^{LW}\gamma_{L}^{LW}\right)^{1/2} + \left(\gamma_{S}^{+}\gamma_{L}^{-}\right)^{1/2} + \left(\gamma_{S}^{-}\gamma_{L}^{+}\right)^{1/2} = \frac{1}{2}\left(1+\cos\theta\right)\gamma_{LV}$$

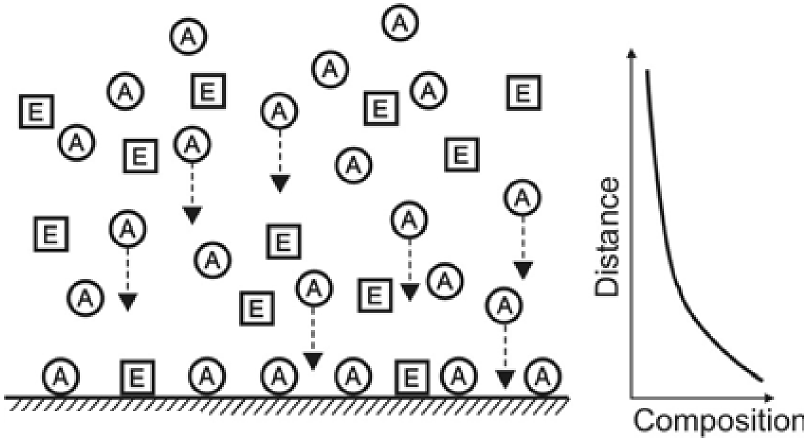
Results for GI and MZ coated steel

Coating type	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ_s (mJ/m^2)	γ_s^+ (mJ/m^2)	γ_s^- (mJ/m^2)
GI	30.1	6.1	36.7	0.6	6.3
MZ	31.8	5.4	37.2	1.1	6.4

- Only small differences in surface energy contributions between GI and MZ coated steel
- MZ slightly more acidic than GI despite higher Mg fraction at surface
- Differences in adhesive strength between GI and MZ is not caused by different wetting behavior

Chemical interactions epoxy and metal oxides

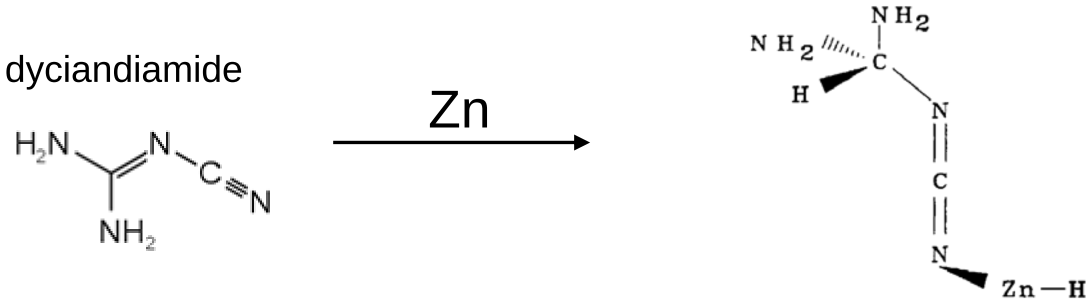




Preferential amine adsorption at metal surface

- Metal surface are covered with acidic –OH functionalities
- This give rise to preferential adsorption of amines (base) for epoxy adhesives

Dicyandiamide is chemically reduced when reacted with zinc



- Coordination to metallic zinc, through the nitrogen lone pair orbital, dicyandiamide act as a π acceptor (amine groups seem unaffected)

- Reaction is governed by the electron donor (basic) properties of the substrate surface

- Little or no reaction possible on iron, zinc oxide and aluminum contaminated steel

- Preferential dicyandiamide adsorption give rise to curing agent gradient at surface

Nitrogen concentration fractured epoxy at surface as determined with EDX

Substrate	Element Line	Net Counts	Net Counts Error	Weight %	Weight % Error	Atom %	Atom % Error
GI:	***N K***	899	+/- 276	5.59	+/- 1.72	5.24	+/- 1.61
MZ:	***N K***	483	+/- 253	3.37	+/- 1.77	3.09	+/- 1.62
PTFE:	***N K***	233	+/- 253	1.68	+/- 1.83	1.59	+/- 1.72

- Nitrogen concentration GI>MZ>PTFE
- Error for N is very large. EDX not very suitable for low mass elements
- XPS measurements to further clarify epoxy curing at interface

Influence surface treatments on wetting and adhesive strength MZ

- 3 treatments have been selected:

  - Uv ozone treatment (5 mins)

  - Alkaline etching (5 min 150 gL^{-1} KOH)

  - Slow cooling of bonded specimen to enable relaxation of residual stresses

MZ treatment	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ_s^{tot} (mJ/m^2)	Bond strength (N)	Work of adhesion (kNmm)
Heptane degreasing (reference)	31.8	5.4	37.2	4823	50.3
UV ozone	28.3	42.4	70.7	4930 (+2.1%)	59.5 (+18.3%)
Alkaline etching	27.3	21.8	49.1	4963 (+2.9%)	64.9 (+29.0%)
Stress relaxation	31	6.7	37.8	4945 (+2.5%)	63.9 (+27.0%)

Influence surface treatments on wetting and adhesive strength MZ

- All selected treatments show an increase in bond strength and an even more remarked increase in work of adhesion
- No clear relation was found between bond strength and surface tension
- All failed samples showed an adhesive failure

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Conclusion

- Surfaces of GI and MZ coated steels are chemically different
- GI performs better in single lap-shear tests than MZ coated steel
- Fractured surfaces of GI show more cohesive failure
- Fractured surfaces of MZ show more adhesive failure
- Differences in adhesive strength between GI and MZ could not be explained by different wetting behavior
- In general preferential adsorption of amines (curing agent) occur at metal surfaces when bonded with epoxy adhesives

Future Work

- Measure dicyandiamide adsorption FTIR with XPS
- XPS on tested lap-shear samples to study curing behavior
- Influence of salt spray on adhesive strength