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Initial stages of localized corrosion at cut-edges of adhesively bonded Zn and Zn-Al-Mg galvanized steel



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ABSTRACT

The mechanisms of the initial stages of localized corrosion at cut edges were investigated for adhesively bonded Zn (Z) and Zn-Al-Mg (ZM) galvanized steel. The results provided strong evidence for the localized nature of corrosion of galvanized coatings at the cut edges and at the adhesive/zinc interface. In both cases a defined localized corrosion attack on zinc in Z sample was observed. On the contrary, in the case of the ZM specimen both zinc solid solution and eutectics exhibited local corrosion. The local attack at the adhesive/Z(ZM) interface was correlated with an anodic undermining process. It develops near the cut-edge surface and at the buried deep adhesive-zinc interface and results in adhesive disbonding in the buried interface. The electrochemical studies revealed that the corrosion kinetics at the metal cut-edges decreases during immersion, which could be due to formation of corrosion products on both steel and zinc surfaces.

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1. Introduction

The automotive industry puts strict demands for safety, comfort and environmental friendliness of vehicles. One of the directions being currently addressed by these demands is the improvement of adhesive bonding technology and in-service performance of adhesive joints especially in load bearing structures. Every year the entire transport sector in the EU uses around 250,000 tons of adhesives [1], and this number is expected to grow in future.

Application of adhesives for metals bonding offers benefits such as improved fatigue resistance, vibration damping properties and sealing of joints [2–4]. Most importantly, adhesively bonded metallic parts are not susceptible to galvanic corrosion [3,4]. Therefore different automotive body parts made of steel, light alloys and composites may be joined with adhesives. Adhesive formulations may include active additives which provide resistance to water penetration and confer additional corrosion protection to the joined metals during exposure to harsh environmental conditions [2,5]. Among different metals, adhesively bonded galvanized steels are used in various applications where structural bonding is of crucial importance, e.g. automotive, house hold, ship building etc.

http://dx.doi.org/10.1016/j.electacta.2016.06.045 0013-4686/© 2016 Elsevier Ltd. All rights reserved. Conventional hot deep galvanizing coatings (HDG) on steel include some fraction of aluminium (below 1%) which prevents the diffusion of iron into the zinc layer and formation of iron-zinc intermetallics [6]. Alloying zinc with some quantities of aluminium and magnesium was reported to improve corrosion resistance of such coatings [7–13]. The aluminium and magnesium content in zinc coatings may vary from 0.2 to 11.0 wt.% and from 0.1 to 3.0 wt. %, respectively, in commercially available galvanized steels [14–18]. Although zinc galvanizing coatings offer good corrosion protection during atmospheric exposure, zinc corrosion is much higher when a zinc galvanizing coating is galvanically connected to steel especially with unfavourably high cathodic to anodic ratio. A cut-edge assembly is a common example of such situation.

The corrosion behaviour of zinc galvanized steel cut-edges and zinc-iron galvanic couples has been previously studied in literature using various methods such as Scanning Vibrating Electrode Technique (SVET), local potentiometry, local polarization, current potential measurements and others [19–26]. The cut-edge corrosion may strongly depend on the composition of the zinc alloy coating. For example, the addition of small amounts of Mg (up to 0.05%) to 4.5%Al+95%Zn alloy increases the zinc corrosion rate at galvanized steel cut-edges in 5% NaCl solution [23]. The Mg addition increases the fraction of primary zinc dendrites, which act as active corrosion sites. In contrast, the use of zinc alloys with higher Mg content (Zn-15 Mg, Zn-5.8Mg, Zn-1.5Al-1.5Mg) reveals

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lower corrosion rate at the cut-edges compared to that found in conventional hot deep galvanized steel cut-edges [24,25]. However, the performance of zinc alloys strongly depends on the testing conditions such as concentration of corrosive solution, solution composition, exposure time etc. Corrosion products form on steel cut-edge surface due to high pH formed in the course of the oxygen reduction process [20]. It is accepted that the corrosion products such as $Zn_5(OH)_8Cl_2$ (simonkolleite), LDH (layered double hydroxides) and $Zn(OH)_2$ may decrease the oxygen reduction reaction kinetics on steel surface and, consequently, reduce corrosion at cut-edges [22,26].

The cut-edge corrosion may negatively affect the stability of the interface between adhesive and galvanized steel and cause delamination of the adhesive layer. The studies employing scanning Kelvin probe revealed that the cathodic delamination mechanism of polymeric coatings from steel substrates plays a major role in coating de-adhesion [27–29]. However, the anodic mechanism of delamination is dominant for complete automotive paint systems as these paints can form a significant barrier to oxygen diffusion [30]. Toughened adhesive layers have also low oxygen permeability and therefore can be subjected to the anodic mechanism of delamination [31]. Recent results by Prosek et al. have shown that coil coated HDG and Zn-Al-Mg galvanized steel develop preferably an anodic mechanism of delamination from cut-edges [24]. The anodic delamination process is more favourable in the case of Zn-Mg alloy coatings, since they have lower kinetics of the cathodic process in comparison to pure zinc [32]. HDG substrates coated by polymeric films show the cathodic delamination mechanism starting from a defect in the polymeric laver down to the zinc [27.33]. However, the mechanism of paint delamination may involve both anodic undercutting and cathodic delamination in front of the undercutting, starting from defects formed in the paint down to the steel surface in the case of painted galvanized steel [28].

Among the available studies on adhesively bonded substrates some issues remain uncertain. For example, it is not completely clear how the initial localized corrosion and the disbonding processes develop on adhesively bonded galvanized steel cutedges and at the adhesive/zinc interface. In the literature the cutedge corrosion often has been described with limitations associated with long-time tests and lack of information on microstructural level, which may hinder the meaningful details of initiation of localized corrosion and its progress. In addition, there is no smooth transition between studies of initial localized corrosion of zinc alloy coatings and degradation of the metal adhesive interface performed at micro and macro scale.

This work was focused on understanding the initial steps of corrosion at the cut-edges of adhesively bonded Zn and Zn-Al-Mg galvanized steel substrates. The main objectives were to reveal the initial corrosion sites and their preferable location using an in-situ AFM and microstructural analysis, and to evaluate the corrosion kinetics at the cut-edges by electrochemical methods.

2. Experimental

2.1. Materials

Two types of galvanized steel substrates were used, namely Z (zinc hot dip galvanized steel) and ZM (Zn-Al-Mg galvanized steel). The galvanizing coating on Z sample contained around 99.5 wt.% of zinc and had a weight around 100 g/m^2 . ZM substrate was coated by Zn-Al-Mg alloy containing approximately 1.5% of Al and 2.5% Mg with a coating weight around 100 g/m^2 . The samples (Z and ZM) have an average thickness of the galvanized layer about 7 and 7.5 μ m and an average roughness (R_a) about 1.6 and 1.2 μ m respectively. Prior to use, the samples were cleaned in ultrasonic bath using n-heptane, 2-propanol and absolute ethanol during 10 min at each step, then dried in a flow of air and stored in a desiccator. Fresh 0.001 M NaCl solution (pH~6.2) was used as corrosive medium.

2.2. Adhesive

A model hot curing adhesive formulation without anticorrosion pigments and adhesion promoters but with good mechanical properties (tensile strength c.a. 37 MPa) was supplied by SIKA. The chemistry of this product is based on toughened epoxy.

2.3. Sample preparation

The adhesive has been applied onto the galvanized steel substrates by squeezing adhesive on the centre of a steel sample strip. Afterwards the samples were covered with a TeflonTM sheet and pressed with a mechanical press at a pressure around 3-5 bars. The adhesive thickness was around $250 \,\mu\text{m}$ and was controlled by hardened steel spacers during the adhesive application and pressing procedure. The prepared samples were cured during 20 min at 170 °C. The sample temperature was monitored by a thermocouple touching the metal surface. The prepared samples were cut into 1 cm² pieces and the zinc coating from the side opposite to the adhesive layer was eliminated with SiC paper in 2propanol. The adhesively bonded samples were embedded in mounting resin (as indicated in Fig. 1). A side perpendicular to the adhesive/zinc/steel sandwich was abraded down to 4000 grit SiC sand paper and then polished using oil based diamond pastes down to 1 µm. The samples were cleaned after polishing in 2propanol in ultrasonic bath during 5 minutes and dried in a flow of warm air. Prior to investigation the samples were etched in 0.5 wt. % solution of nitric acid in ethanol during 1 second and then immediately washed in 2-propanol and dried in order to reveal the microstructure of the polished cut-edges and to remove possible layers of deposits from the surface. A protective varnish was applied on the other sides of the sample in order to confine the exposed area (Fig. 1).



Fig. 1. Schematic representation of the cut-edge of adhesively bonded galvanized steel.

2.4. AFM and in situ measurements

A Digital Instruments NanoScope III atomic force microscope (AFM) system with ExtenderTM Electronic Module was used for acquisition of topography and Volta potential maps. The topography was acquired in tapping mode when the tip was in intermittent contact with the substrate. The AFM was operated in the interleave mode with two pass scans in scanning Kelvin probe force microscopy (SKPFM) mode. During the first pass surface topography was acquired. During the second pass the tip was lifted up from the surface by 100 nm, then an ac voltage bias of 5V was applied between the tip and the sample to induce oscillations of the cantilever. Using a nulling technique, the Volta potential difference between the sample and the tip was measured over the whole surface. Topography and VPD maps with surface area $20 \times 20 \,\mu m$ were acquired. It was assumed that the Volta potential difference measured by SKPFM in air is related to the difference between the work function of the probe and the surface. For all SKPFM measurements silicon probes covered with Cr/Pt layers were used.

A Pico LE AFM with 2100 controller (Molecular Imaging) and equipped with a 90 \times 90 μ m open loop scanner was used for in situ AFM measurements of cut-edges during immersion in a corrosive electrolyte. In situ measurements were performed with AFM probes acquired from App Nano (model ACT). The probes were made of doped Si, with the following characteristics: tip pyramid height 14–16 µm, tip radius < 10 nm, 300 kHz resonance frequency, spring constant around 37 N/m. Such AFM probes demonstrate an enhanced performance both in air and in liquids. AFM maps with the size of $20 \times 20 \,\mu\text{m}$ with 256 by 256 data points were acquired. The step size (resolution) was around 78 nm. In-situ measurements were performed in a liquid cell which consisted of an O-ring firmly pressed to a flat sample, forming a small pool with the volume around 0.7 ml. A preliminary surface topography was acquired in air in semi-contact mode. AFM in situ measurements were started after injecting an electrolyte into the liquid cell. AFM was operating in semi-contact mode in liquid which allowed tracking the surface topography during immersion in the corrosive solution. A resonance peak of the cantilever in liquid (~120-150 kHz) has been selected for the topography measurements. The samples were washed after the in situ measurements with deionized water during 10 seconds, dried in a flow of air during 30 sec and stored in a desiccator.

The same AFM equipment was used for the Z and ZM sample topography measurements under polarisation. The setup consisted of the Pico LE AFM system equipped with the liquid cell and an Autolab PGStAT 302 N potentiostat. In order to reduce the IR drop effect a 0.005 M NaCl solution was used for electrochemical AFM measurements. The electrochemical cell consisted of a flat sample made of Z or ZM substrate which acted as a working electrode, an Ag/AgCl wire as a reference electrode and a Pt wire as a counter electrode. The Z and ZM flat surfaces were prepared by polishing the galvanized coating down to 1 grade diamond paste and cleaned in 2-propanol. During immersion the open circuit potential (OCP) of the samples was measured until stable values were obtained around -0.98 V vs. saturated calomel reference electrode (SCE). Then an anodic potential +40 mV vs. OCP was applied and in situ AFM measurements were performed under anodic polarisation.

2.5. SEM/EDS measurements

Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) studies were performed by a Hitachi FE-SEM system SU-70 equipped with a Brucker EDS detector

2.6. SVET measurements

Scanning vibrating electrode technique (SVET) measurements were carried out using an Applicable Electronics (USA) equipment. The technique is based on the measurement of potential gradients in a solution associated to ionic fluxes created by oxidation and reduction reactions on metallic substrates. The SVET microprobe presents a spherical platinum black tip with the diameter of 10 μ m. The probe vibrated perpendicularly to the surface with the amplitude of approximately 20 μ m. The measured voltage differences were converted to current densities (normalized for 1 cm²) by a calibration routine performed with a point current source (microelectrode with a tip of ~3 μ m) driving a current of 60 nA at 150 μ m distance from the vibrating probe. Maps of 40 × 40 data points were obtained with the probe vibrating at a distance of 100 μ m above the sample surface during immersion.

2.7. EIS and DC polarisation measurements

Electrochemical impedance spectroscopy (EIS) measurements were performed on cut-edges using a GAMRY potentiostat PCI4/750. A three electrode electrochemical cell was employed for the measurements comprising the working electrode (cut-edge) with a surface area around 0.11 cm², a platinum foil (surface area around 1 cm²) as counter electrode and a saturated calomel electrode (SCE) immersed in a salt bridge filled with 1 mM NaCl solution. The internal solution of the salt bridge was refreshed between the measurements in order to avoid an excessive contamination of the working electrolyte. The impedance measurements were performed in the frequency range of 10 kHz to 0.05 Hz, with 7 points per decade and 10 mV RMS amplitude.

DC polarisation measurements were performed using the same equipment. The measurements were performed in 0.005 M NaCl solution on polished (down to 1 grade diamond paste) Z, ZM and steel flat samples acting as a working electrode with an area of 1 cm². A SCE electrode equipped with a Luggin capillary was used as a reference electrode and a Pt spring with around 2 cm² surface area was used as a counter electrode. The OCP potential was acquired during 30 min before polarisation. Afterwards, current-voltage curves were acquired with a scan rate of 1 mV/sec in anodic (Z and ZM) and cathodic (steel) directions.

3. Results

3.1. Characterization of the cut-edges before immersion

The microstructure of the Z and ZM cut-edges is shown in Fig. 2. Zinc coating on Z sample has a thickness around $7-9 \,\mu\text{m}$. The bulk zinc matrix shows a uniform contrast in SEM maps. The interface between zinc and steel is enriched with Al. Its composition can be described as Al₅Fe₂ [34]. This layer inhibits the diffusion of iron to the zinc rich layer and the formation of iron containing phases [35]. The zinc solid solution phase on the Z sample is mainly composed of Zn (Fig. 2c). The ZM cut-edge demonstrates different microstructure compared to Z one. The SEM micrograph of ZM sample shows several zones having different contrast and microstructure in the zinc layer (Fig. 2b). The zinc solid solution phase can be identified in the bright places (Fig. 2b,c #2). The zones which have a somewhat darker contrast (Fig. 2b #3,4) are composed of a binary or ternary eutectic solution of zinc, aluminium and MgZn₂ [7,13]. The binary eutectics have larger MgZn₂ lamellas compared to ternary eutectics (Fig. 2b). EDS can clearly show the difference in intensity between the Mg peak and the Al one on the spectra acquired on binary and ternary eutectics (Fig. 2c #3,4).

3.2. Corrosion in NaCl solution

3.2.1. AFM characterisation of the cut-edges

In situ AFM measurements were done during immersion in 0.001 M NaCl solution in order to characterize the initial stages of the corrosion attack. A low concentration of NaCl solution was chosen since the zinc laver degradation rate at higher NaCl concentrations was too fast. Fig. 3 presents topography maps and profiles acquired on the Z sample cut-edge surface before immersion (a) and during immersion (b,c,d) in NaCl solution. The maps show three distinct regions ascribed to adhesive, zinc and steel (from left to right). The polishing procedure caused some overpolishing of softer zinc surface with respect to more hard adhesive and steel parts (Fig. 3a). After addition of electrolyte in a liquid cell the corrosion process had quickly initiated in some particular zones on the zinc layer. The shiny zinc layer before immersion quickly turned black during the in situ tests (not shown). This indicates the rapid corrosion process occurring during immersion. Such changes can be attributed to dissolution of metal and formation of a corrosion product layer at the beginning of immersion. The AFM map acquired after 24 min of immersion depicts dissolution of the zinc matrix and formation of small pits up to 1 µm deep, marked by black arrows on the image (Fig. 3b). During immersion the dissolution depth was progressively increasing deeper into the zinc layer (Fig. 3c,d,e). The maximal dissolution depth at the end of the immersion was around 1 μ m as indicated on profiles Fig. 3c,e. However, in some other places of the maps the trench depth could reach around $1.5 \,\mu m$ (see the bottom of the image). Fig. 3d. The changes in topography suggest that pits form on the zinc surface in some active spots.

In situ AFM measurements on the ZM cut-edge were performed in a similar fashion as for Z sample. The first topography map

shows the ZM substrate cut-edge before exposure to NaCl solution (Fig. 4a). The surface topography shows a zone indicated by an arrow (Fig. 4a), which is attributed to the ternary eutectic phases. The microstructure of this zone is very similar to the one that corresponds to the ternary eutectics (Fig. 2b). The zinc solid solution zone is located below the contour line (Fig. 4a). The black line profiles on the AFM maps before (Fig. 4a) and during (Fig. 4b.c. d) in situ measurements identify the same zone on these maps. During short term in situ immersion a rapid localized corrosion process started on the zinc layer of the ZM sample. After 15 min of immersion the map shows two local pits on the surface (Fig. 4b). The local corrosion process initiated near the eutectic zone in the upper part of the image while the second local corrosion process developed on a zinc solid solution zone in the bottom part (Fig. 4b). The AFM map presented in Fig. 4b and topography profiles on Fig. 4e demonstrate that the corrosion products precipitate on steel surface on the right part of the investigated area. This is consistent with the fast corrosion process developed on the cut-edge. The pits in the Zn layer represented by a darker zone in the upper and lower parts of the topography images are growing continuously (Fig. 4b,c, d). At longer immersion time the corrosion process progressed through the Zn matrix and a deeper trench more than 1.5 µm (shown by an arrow) formed (Fig. 4d,e). Dissolution of the zinc layer continued at longer immersion time in the galvanized layer close to adhesive/zinc interface (Fig. 4d). It should be noticed that the eutectic zone close to the adhesive has been slightly corroded by the end of immersion (Fig. 4d). Initially, the topography across the zinc cut-edge surface was flat and by the end of immersion the topography became rough and uneven (Figs. 4a.d). However, the topography profiles presented in Fig. 4e did not show pits on the eutectic zone close to adhesive.



Fig. 2. SEM micrographs of Z (a) and ZM (b) adhesively bonded galvanized layer cut-edges and EDS spectra (c) of the selected regions on both micrographs.



Fig. 3. AFM topography maps made on cut-edge of adhesively bonded Z substrate before immersion (a) and during 24 min (b), 1 h 5 min (c), and 2 h (d) immersion in 0.001 M NaCl; figure (e) presents evolution of topography across the black lines profiles drawn in the same zones on AFM maps. Black arrows indicate local pits on zinc layer. AFM images show adhesive on the left side, zinc in the middle and steel on the right.

X distance, micron



Fig. 4. AFM topography maps made on cut-edge of adhesively bonded ZM substrate before immersion (a) and during 15 min (b), 41 min (c) and 2 h 08 min (d) immersion in 0.001 M NaCl; figure (e) presents evolution of topography across the black lines profiles drawn in the same zones on AFM maps. Arrows indicate local pits in zinc layer. AFM images show adhesive on the left side, zinc in the middle and steel on the right.

X distance, micron

2h 8 min

-1.4

The above experiments highlight typical local corrosion features found during the in situ AFM tests. Cut-edges can also show larger pits consuming the entire width of the zinc layer and, in many cases, the corrosion product precipitates on both the Z and ZM zinc layer surfaces during immersion (not shown). One of the important aspects of the localized studies concerns the corrosion of the eutectic phases. The analysis of the localized corrosion behaviour on different ZM cut-edges did not clearly confirm the preferential formation of pits on eutectic phases. Another interesting point is related to the localized pitting activity arising at zinc solid solution zones. This is inconsistent with the higher corrosion activity of the eutectic phases containing the most active element Mg and contradicts with the studies reported in Ref. [36]. Additional AFM experiments were performed on model galvanized coatings of the Z and ZM samples to clarify these points.

3.2.2. In situ AFM measurements on model Z and ZM surfaces under anodic polarisation

For these experiments, Z and ZM galvanized coatings were polished to approximately $1-3 \mu m$ in depth. The polished surface was microstructurally similar to the layer of zinc at the cut-edges. In order to cause anodic dissolution of the zinc coatings, a potential of +40 mV vs. corrosion potential of the sample was applied. This potential difference was similar to the polarisation of zinc coatings by steel as follows from the polarisation measurements presented in Fig. 5f. The intersection between the polarisation curves made on steel and polished zinc coatings is located approximately 40 mV above the corrosion potential of the Z and ZM galvanizing coatings (Fig. 5f).

Fig. 5 presents evolution of topography before and during polarisation of the Z sample surface. The black line profiles, shown on AFM maps, were drawn through the same place. The arrow indicated in Fig. 5b shows the moment during the scan when the

polarisation started. The AFM map (upper part) revealed an immediate localized pitting corrosion of the Z surface after the polarisation was applied. The shape of the formed pits is similar to those found on the Z cut-edge (Fig. 3). During immersion, the local pits grow deeper into the zinc surface (Fig. 5e). At longer immersion time (>30 min) the zinc surface shows more corrosion spots and presents visible dissolution of metal matrix (not shown).

The localized corrosion activity of the ZM sample on a selected zone is presented in Fig. 6. The location before immersion is shown on the topography and Volta potential maps in Fig. 6a and b respectively. The area in the middle of the images is attributed to ternary eutectics region. This place has lower Volta potential level (dark area) compared to the surrounding zone of zinc solid solution separated by contour profiles (light area), Fig. 6b. Moreover, the analysis of such area after corrosion by SEM/EDS (not shown) has confirmed the presence of Al in the eutectic zone. Therefore such zone can be correlated with ternary eutectic.

Evident metal dissolution of the metal matrix can be seen on the AFM map after 4 min of polarisation (Fig. 5c). The AFM topography profiles before and during the immersion were levelled relatively to the zero level located on the uncorroded zinc surface (Fig. 6f). These profiles show visible dissolution of eutectic phases and also local corrosion attack at the zone of zinc solid solution (Fig. 6f). The topography map presented in Fig. 6d clearly shows corrosion of both the eutectic zone and local corrosion of the solid solution zone. However, the dissolution process is not progressing uniformly on the zinc solid solution zones. After 16 min of immersion the dissolution of zinc solid solution becomes visible on the left side of the image (Fig. 6e,f). With longer immersion (22 min) the AFM profile shows evidence of zinc solid solution dissolution on the right side (Fig. 6f).

These experiments have confirmed the localized nature of corrosion attack on Z and ZM samples. The corrosion process



Fig. 5. AFM topography maps of polished Z galvanized coating before immersion (a) and during immersion in 0.005 M NaCl: 3 min (b), 22 min (c), 35 min (d); figure (e) presents evolution of topography across the black lines profiles; figure (f) presents cathodic polarization curve on steel and anodic polarisation curves on Z and ZM samples.



Fig. 6. AFM topography (a) and SKPFM (b) maps of polished ZM galvanized coating before immersion and during immersion in 0.005 M NaCl: 4 min (c), 9 min (d), 22 min (e); figure (f) presents evolution of topography across the black lines profiles.

develops in a similar way as it was shown earlier in the cut-edge experiments (Paragraph 3.2.2). More specifically, the corrosion locus can be located at zinc solid solution (Z sample) and at both eutectic phases and zinc solid solution in the case of the ZM system.

3.2.3. SEM/EDS characterisation of the cut-edge surface after corrosion The images (Fig. 7a,c) show general view of the Z and ZM cutedges after corrosion. Semicircle contour lines demonstrate the distribution of corrosion products along the steel surface with the anodically active zinc layers located nearby. AFM measurements



Fig. 7. SEM micrographs of Z (a,b) and ZM (c,d) cut-edges after in situ AFM measurements.

were performed on the anodically active zones shown by black squares (Fig. 7a,c). Fig. 7b,d presents zoomed regions of cut edge surface where AFM measurements were performed. The surface of zinc layer reveals well defined corrosion attack. SEM images also display several cracks on the corroded zinc layer and near the adhesive/zinc interface after corrosion (Fig. 7b,d). Most probably mechanical stresses developed inside the corrosion products layer during drying of the samples in air or in the SEM chamber inducing the contraction of corrosion products and, consequently, the appearance of cracks. The inspection of other regions along the zinc cut-edge also showed cracks in various parts of the corroded zinc layers in Z and ZM samples (not shown).

The EDS analysis of the corroded cut-edge zones (Fig. 7b,d) revealed the decrease of Zn and Mg (in the case of the ZM sample) and the increase of Cl, O and Al signals intensity with respect to the uncorroded zones (not shown). The changes of the at.% of different elements are presented in Table 1. The EDS spectra did not reveal any measurable Mg levels on the corroded ZM cut-edge. This confirms that Mg-rich phases dissolve during the cut-edge immersion. On the other hand, the Al signals have increased on Z and ZM samples after corrosion (Table 1). Such increase may be caused by enhanced stability of Al-containing phases towards the

Table 1

At. % of major elements and elemental ratios obtained on zinc interface after in situ immersion and on undamaged Zn layers. (- states for not detectable elements).

	Z		ZM	
	corroded	blank	corroded	blank
Al	0.9	_	5.6	2.9
Mg	-	-	-	1.0
Zn	37.4	81.9	49.1	77.5
0	51.6		41.1	
Cl	3.7	-	1.45	-
Zn/O	0.72		1.19	
Al/Zn	0.023		0.114	0.037

dissolution from the zinc layer and by the formation of stable Al corrosion products on the galvanized layer. Signals of O and Cl have increased after corrosion, indicating the formation of corrosion products (Table 1). The ratio of Zn:O was around 0.8–1.2 on the sample after corrosion of Z and ZM galvanized layers (Table 1). Most probably it indicates the presence of Zn oxyhydroxides as corrosion products. However, the presence of the Cl signal after corrosion may indicate the formation of more complex corrosion products of zinc.

An additional analysis of the ZM cut edge after corrosion has been done to clarify details of the eutectic phase corrosion. SEM and EDS maps were acquired on the ZM samples perpendicular to the plane of the cut-edge as depicted on the sketch (Fig. 8). The SEM micrograph denotes the eutectic zone in the middle highlighted by a contour line and two zinc solid solution zones located in the top and bottom parts of the image. The composition of the solid solution zone was similar to that presented in Fig. 2c (zone #2). The corroded eutectic zone was ascribed to ternary eutectics which had similar composition as the zone #4 indicated in Fig. 2c. The eutectic zone appears to be significantly corroded compared to the zinc solid solution zones. This correlates with the increase of the O signal and the absence of Mg signal as shown in Fig. 8b,d. The absence of Mg clearly demonstrates the selective dissolution of this element from the eutectic phase. On the other hand, Zn lamellas stayed relatively intact inside the ternary eutectic region (Fig. 8e). The EDS analysis also demonstrates the accumulation of Al and O signals in the eutectic zone (Fig. 8c). This evidences the formation of corrosion products in the eutectic phase.

3.2.4. SEM/EDS characterisation of the zinc/adhesive interface

In spite of the extensive characterisation of the cut edges after exposure to NaCl solution some details of the corrosion attack at the adhesive/zinc interface remain hidden below the adhesive layer. In order to clarify how short term cut edge corrosion impacts the interface degradation some additional microstructural studies



Fig. 8. SEM micrograph and maps of O, Al, Mg and Zn elements of ZM cut-edge immersed for 2 hours in 1 mM NaCl. Ternary eutectic region is highlighted by a black line. The SEM observation plane is schematically presented on the right inset scheme.



Fig. 9. SEM and EDS maps of the corroded Z sample zinc surface after adhesive removal. The SEM observation plane is schematically presented on the sketch.

have been done. Figs. 9 and 10 present SEM images and EDS maps acquired on the Z and ZM galvanizing coating interface after the adhesive was detached as was shown on the sketch. After immersion, the zinc coatings close to the cut-edge were locally corroded to a depth about $20-30 \,\mu\text{m}$ on both the Z and ZM samples (Figs. 9 and 10). The corrosion zone can be correlated with the depletion of zinc (Fig. 9d). On this zone the EDS revealed high concentration of Cl and O elements (Figs. 9b,c and 10b,c). In some areas O and Cl signals may be found to a depth about $80 \,\mu\text{m}$ demonstrating that the corrosion process may significantly extend in the buried zinc adhesive interface. This evidently shows that corrosion products can form at a high depth from the cut-edge.

Moreover, Mg signal could not be detected on a large distance from the cut edge on the ZM sample (Fig. 10d). Consequently, such depletion reflects the higher corrosion susceptibility of the eutectics at the adhesive/zinc interface. These results indicate a deeper corrosion attack compared to what was observed at the cut edges by in situ AFM and SEM/EDS.

Microstructural analysis has also revealed an initial localized corrosion at the zinc-adhesive interface as indicated in Figs. 9a, 10a. Fig. 11 presents the uncorroded (a,b) and corroded zinc coatings of Z and ZM cut-edges (c,d) after adhesive removal. The pictures of the corroded surface were acquired at the depth about 50–60 μ m from the cut-edge surface. After corrosion the Z



Fig. 10. SEM and EDS maps of the corroded ZM sample zinc surface after adhesive removal. The SEM observation plane is the same as indicated in Fig. 10.

galvanized surface depicted local dissolution zones found on both zinc grains and grain boundaries (Fig. 11c). On the other hand, local corrosion attack was revealed on both eutectic and zinc solid solution regions on the ZM sample (Fig. 11d).

3.2.5. Electrochemical investigation of the cut-edge corrosion

Fig. 12 shows the ionic current density distribution determined by SVET on the Z and ZM cut-edges during 5 min, 1 hour and 2 hours of immersion in 0.001 M NaCl solution. The initial maps show high anodic currents reaching values up to 65 and 72 μ A/cm² (Fig. 12a,e). The anodic current distribution shows several active local zones displaying high currents values. During immersion the number of active anodic zones and the magnitude of current density can change (Fig. 12b,c,f,g). Small pits giving low anodic currents might not be detected by SVET, which results in errors in the determination of the total anodic activity which can be lower than the cathodic one [37]. In contrast to that, the cathodic activity is homogeneously distributed on adjacent steel surface where the observed ionic current densities reach high values about -60 to $-67 \,\mu$ A/cm² (Fig. 12a,e). The cathodic activity also decreases with time presenting smaller values in the case of the Z sample compared to the ZM one. By the end of immersion optical pictures display a layer of corrosion products on steel surface cut edges (Fig. 12d,h).

In evaluation of the corrosion kinetics, it is more convenient to present the integrated SVET current values normalized per unit of area of metal. Both anodic and cathodic currents were integrated in order to find the total ionic current activities and show the evolution of the corrosion kinetics over time (Fig. 13a). It can be

seen that the total ionic currents generated on the ZM sample are higher than on Z one, which suggests a slightly higher corrosion activity of the ZM sample. In both cases the activity decreases with the immersion time. A more detailed analysis of the localized corrosion behaviour on the Z and ZM cut-edges is presented in Fig. 13b. The figure shows evolution of the current profiles drawn through the black lines as indicated in Fig. 12. It can be seen that the anodic activity on zinc significantly decreases with time (Fig. 13b). However, the steel area close to the zinc edge shows high levels of cathodic activity (Fig. 13b). Therefore a sudden anodic current decrease may be consistent with the deposition of a corrosion products layer on zinc as it was shown in Figs. 7b,d, 9, 10. Such layer may locally block the zinc dissolution thereby reducing anodic ionic currents as was shown on SVET ionic current maps and current profiles (Figs. 12 and 13b).

The impedance spectra of the Z and ZM cut-edges during immersion are presented in Fig. 14. The initial impedance spectra show one clear time constant at low frequencies. This relaxation process is attributed to polarisation resistance and double layer capacitance, which represents an active corrosion process on a cut-edge. In addition, a new time constant appears on the spectra at higher frequencies during immersion (Fig. 14). This time constant has become more defined by the end of 2 hours of immersion and it can be attributed to a growth of corrosion precipitates on the cut-edge surface. The impedance spectra after 2 h of immersion were fitted with an equivalent circuit composed of two time constants in cascade. The model describes a corrosion product film which deposits on a part of the metal surface and a corrosion process. The χ^2 parameter of fitting was around



Fig. 11. SEM images of uncorroded Z (a), ZM (b) zinc surface and corroded zinc-adhesive interface Z (c) and ZM (d) after adhesive removal.



Fig. 12. Ionic current maps and optical images acquired on Z (a.b.c.d) and ZM (e,f,g,h) cut-edges during immersion in 0.001 M NaCl solution. Immersion time; 5 min (a, e), 1 hour (b, f), 2 hours (c, d and g, h); the ionic currents are in the units μ A/cm².

 7×10^{-4} indicating an appreciable quality of fitting and therefore confirming the applicability of the used model. The fitting lines are shown on the EIS spectra of the samples after 2 hours of immersion (Fig. 14). During 2 hours of immersion the polarisation resistance increased from around 1500 to 3000 Ohm cm² and

from 1000 to 2500 $\Omega \cdot \text{cm}^2$ on Z and ZM cut edges, respectively. At longer immersion time (ca. 6 h) the same resistances further increased to 5000 $\Omega \cdot \text{cm}^2$ and 3300 $\Omega \cdot \text{cm}^2$. The corrosion products resistance grows slightly during 0.5–2 h of immersion on the Z sample from 160 to 510 $\Omega \cdot \text{cm}^2$ and on the ZM it stays



Fig. 13. Integrated total ionic currents activity (a) and ionic current profiles (b) on Z and ZM samples cut-edges acquired through black profiles shown in Fig. 12.

around $300-280 \,\Omega \cdot cm^2$. However, at longer immersion (ca. 6 h) this resistance drops at both Z and ZM cut edges.

4. Discussion

The experimental results presented above cover the several main points of this study such as: 1. Development of local corrosion attack during Z and ZM cut-edge corrosion; 2. Local corrosion attack at adhesive/zinc coating interface; 3. Influence of the corrosion products on the corrosion kinetics. The sections below summarise and discuss the results.

4.1. Localized corrosion on cut-edges and model galvanizing coatings

The cut-edge corrosion presents a complex scenario involving a galvanic attack [38]. In a galvanic couple of zinc and steel immersed in corrosive solution, the steel supports the cathodic process of oxygen reduction reaction (reaction (1)). The cathodic process on the steel surface polarises the zinc layer and accelerates the anodic process of zinc dissolution (reaction (2)). Zinc cations can migrate towards the cathodic area where they react with the hydroxyl anions and precipitate as zinc oxide/hydroxide (reaction (3)).

$$O_2 + 4e^- + 4H_2O \to 4OH^-,$$
 (1)

$$Zn \to Zn^{2+} + 2e^{-}, \tag{2}$$



Fig. 14. EIS spectra of Z and ZM cut-edges during immersion in 1 mM NaCl.

$$Zn^{2+} + 2OH^{-} \to Zn(OH)_2 \downarrow, \tag{3}$$

$$MgZn_2 \to 2Zn^{2+} + Mg^{2+} + 6e^-$$
 (4)

The formation of local pits on the zinc galvanized layers is the first step in corrosion at Z and ZM cut-edges. However, the areas and position where local pits form could not be associated with any microstructural features on the zinc layer (Z cut-edge). It seems that the local corrosion was statistically distributed over the zinc. On the other hand, the first visible pits form at the interface between eutectic phases and zinc solid solution and on zinc solid solution at ZM cut-edge (Fig. 4). This finding was surprizing, taking into account the high corrosion susceptibility of the eutectic phases. However the types of attack are different and can be described as a pitting in the case of the solid solution regions and selective dissolution at the eutectic zones. During the first hour of immersion the changes of topography profiles across the zinc layer were consistent with the high corrosion rate of the zinc layer (Figs. 3e and 4e). However, at a later stage (2 h) the change of topography was not prominent. This can be attributed to the surface blocking by corrosion precipitates.

Localized pitting attack has also been found during in situ AFM measurements on the model polished galvanizing coatings under anodic polarisation. The Z sample revealed similar localized pitting attack as in the case of cut edge corrosion (Figs. 3 and 5). On the other hand, both the ternary eutectic phases and the zinc solid solution underwent a corrosion attack on the ZM sample (Fig. 6). The corrosion locus was located on the eutectic phases and at the interface between eutectics and solid solution zones, similar to what was found on ZM cut-edge (Figs. 4 and 6). Polarisation curves recorded for model Z and ZM samples show low anodic slopes suggesting high zinc corrosion rate during polarisation (Fig. 5f).

From the point of view of electrochemical behaviour, simultaneous corrosion of both phases is possible since the anodic polarisation of zinc is sufficient to cause pitting corrosion of zinc galvanizing coatings. At the cut-edges the steel surface area is much larger than that of zinc. Therefore the anodic current density on zinc will be higher which causes corrosion of both eutectics and zinc solid solution phases.

The in situ studies did not clearly show the dissolution of the eutectic phases on the cut edges during immersion. This is due to the fact that the AFM probe has low resolution, in the case of rough samples and large z-range, which does not allow to distinguish the dissolution of small MgZn₂ phases (reaction (4)) during dealloying. Moreover, the corrosion products formed on the zinc layers may hamper the topography analysis. In the course of the AFM experiments a false imaging of topography is created by the layer of corrosion products which hides the zinc dissolution.

The MgZn₂ phase corrosion often results in the formation of holes and trenches as was observed before [36,39]. However, in the present work these features were not found. The attack of the $MgZn_2$ phase (reaction (4)) is reflected in changes of the elemental composition at the cut-edges (Table 1, Fig. 8). Mg signal was not detected because of leaching of soluble Mg²⁺ cations which cannot form stable insoluble hydroxides until pH reaches up to relatively alkaline values [40]. On the other hand, zinc hydroxide precipitation occurs at pH higher than 6.5 (at zinc ions concentration about 0.01 M). Al signal does not decrease on the corroded eutectics (Figs. 8c). It is more likely that Al dissolves anodically and then forms insoluble hydroxides, which are stable in the near neutral pH range (ca. 4-8) in accordance with Pourbaix diagrams [40]. These corrosion products clog the voids in the corroded ternary eutectic phases during the initial corrosion of the ZM cut-edge. Oppositely, only zinc corrosion products form on the galvanizing layer during the Z cut-edge immersion. Although Al corrosion products may improve corrosion resistance of Zn-Al-Mg galvanizing coatings [41], they do not offer an additional corrosion protection during initial corrosion at the Z and ZM cut edges. Electrochemical tests showed higher corrosion of the ZM cut edges compared to Z ones.

4.2. Localized corrosion at adhesive/galvanizing coating interface

The microstructural observation of the galvanizing coating surface after adhesive removal has revealed that the zinc layer near the cut-edge surface was substantially corroded to a depth about 20–30 μ m (Figs. 9 and 10). This corrosion zone was attributed to the first disbonding zone between adhesive and metal. Moreover, a superficial localized dissolution of both zinc solid solution and eutectics was additionally revealed at zinc/ adhesive interface (Fig. 11). The second disbonding zone has been identified at the buried adhesive/zinc interface. The localized attack at the interface can be found preferably below highly active anodic places at the cut-edge. Figs. 9a,c and 10a,c show a high O signal below the cut edge surface and reveal the zone where the localized attack at the interface is found. On the contrary, interface corrosion has not been found below the inactive cutedge surface which did not show any anodic dissolution. Such intact zinc/adhesive interface zones can be seen at the right part of Fig. 9 or the left part of Fig. 10.

It can be suggested that the high anodic activity and ion migration are contributing factors towards the initiation of interface corrosion and deadhesion. Adhesive delamination can be caused by the following factors: chemical (slightly lower pH due to hydrolysis), wet deadhesion (displacing bonds formed between adhesive molecules and passive metal surface) and hydration of a passive oxide film at the adhesive/ zinc interface [42,43]. At high dissolution rates the concentration of ions in the confined zone significantly increases which may cause an excessive osmotic pressure and induce delamination [43].

The observed interfacial corrosion behaviour can be correlated with the anodic undermining process on the zinc/adhesive interface. In this process a cathode is located close to the cutedge surface and the anodic zinc dissolution zone is in the buried interface. ZM coating has revealed a higher interface corrosion due to the dissolution of the eutectic phases (Figs. 8a, 11d), which provides pathways for corrosive species to reach the buried interface. The observed localized attack close to anodic places may suggest that the osmotic effect coupled with anodic undermining can play a significant role in the initiation of corrosion at the interface of the Z and ZM cut-edges.

4.3. Effect of the corrosion products on the corrosion kinetics at Z and ZM cut-edges

In this part a possible influence of the corrosion products on cut-edge corrosion will be discussed. The total anodic currents in SVET measurements have decreased to around 60% compared to the initial activity on both Z and ZM samples by the end of 2 h of immersion. However, corrosion precipitates on steel have covered less than 25% of the steel area close to the zinc edge on both Z and ZM samples (Fig. 12d,h). The observed total decrease of the anodic currents cannot be explained assuming that the cathodic process is retarded on 25% of the steel area. During immersion some highly active anodic zones show significant decrease in activity at cut edges over time. This effect is related to the formation of corrosion products on the zinc edge, which may increase the IR drop across this layer in the diluted NaCl solution. Both O and Cl elements found on the zinc cut-edges (Table 1) may indicate that oxyhydroxides and Cl containing corrosion products were formed. Based on the EDS analysis and the equilibrium of the zinc species in chloride solution and other literature data [11,22,26,40,44,45] it is possible to assume the formation of simonkolleite $(Zn_5(OH)_8Cl_2)$, apart from zinc oxyhydroxides. It can be suggested that the formed compact layer of corrosion products may decrease the dissolution process on zinc.

On the other hand, EIS results revealed that the corrosion products layer is quickly formed on the galvanised steel cut edge. The resistance of the corrosion products on the cutedges does not significantly increase during 2 h of immersion and drops after longer immersion time, i.e. 6 h. However, the polarisation resistance constantly increases during immersion. In the case that the blocking of corrosion on steel is the only reason for the decrease of corrosion at cut-edges, then the resistance related to the corrosion product layer should increase with time. The inhibition of cathodic activity at cut-edges is sometimes attributed to the formation of a dense protective layer on steel [19,20,25,26]. However, the morphology of the corrosion precipitates on steel, found in this work, looks quite porous (not presented). Besides, during immersion the cathodic zones close to the zinc layer did not show a well pronounced decrease of the cathodic current (Fig. 13b). The analysis of the steel cut-edge surface by EDS after corrosion has not revealed the presence of Cl (not shown) thereby ruling out a possible influence of Cl-containing compounds on the corrosion processes on steel. Therefore, within the frame of this work it is possible to suggest that the decrease of corrosion at the Z and ZM cut-edges may be related not only to blocking of the cathode. In the diluted NaCl solution the anodic activity may also decrease due to the layer of corrosion products formed on zinc.

5. Conclusions

The initial stages of localized corrosion at the cut edges were investigated for adhesively bonded Zn (Z) and Zn-Al-Mg (ZM) galvanized steel. The studies were performed in 1 mM NaCl solution as corrosive medium using localized methods of analysis such as in situ AFM, SVET; and EIS. The changes of the microstructure and elemental composition on the samples after corrosion were studied by SEM and EDS.

The initial localized corrosion attack at the cut-edges was characterised by in situ AFM analysis. The first corrosion pits at the Z cut-edges formed mainly on the bulk zinc layers without any preferential attack on either the adhesive/zinc or zinc/steel at the cut-edge surface. The ZM cut-edge revealed two types of attack at initial stages, namely a strong pitting at Zn alpha phase and selective dissolution at eutectic areas.

The zinc/adhesive interface revealed two main zones where adhesive disbonding occurred during corrosion. The first zone was located near the cut-edge surface where the zinc layer is dissolved to a depth of about 20–30 μ m. The second disbonding zone was located at the buried deep adhesive/zinc interface. In this zone the localized corrosion was found on zinc grains in the case of the Z sample and on both zinc solid solution and eutectic phases in the ZM sample. Such process leads to significantly higher propagation of the disbonded area compared to the one caused by the full dissolution of the zinc layer.

SVET and EIS electrochemical measurements showed the decrease in corrosion kinetics at Z and ZM cut-edges. These results were attributed to the blocking effect of a dense film of corrosion products formed on both zinc and steel surfaces.

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