

Surface and Coating Analysis of Press-Hardened Hot-Dip Galvanized Steel Sheet

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The use of continuous galvanized steel sheet as feedstock material for press hardening leads to components of very high strength levels with classical cathodic corrosion protection. The present work provides an insight into this technology with special focus on surface oxidation and intermetallic phase formation during the austenisation process. For that reason hot dipped galvanized 22MnB5 steel sheets, with a blank thickness of 1.5 mm and an average coating weight of 70 g m^{-2} , were annealed in a temperature range of 400–900°C in steps of 50°C without soaking before quenching in water. Surface and cross-cuts were analyzed by SEM, EDX, and XRD to illustrate the phase formation and the surface changes during thermal treatment. Corrosion behavior was also studied based on electrochemical investigations and an accelerated, cyclic, automotive corrosion tests called VDA, which is a mixture of salt spray test and alternating climate test. It was found that austenisation of galvanized steel sheet causes a significant change of the coating. The generated coating still offers cathodic protection for the steel substrate and has higher corrosion resistance than standard galvanized steel sheet. Surface oxidation also occurs during the press hardening process leading to a surface covered with successively arranged layers of Al_2O_3 and ZnO , containing also further oxidized alloying elements.

1. Introduction

Nowadays automotive industry has to face up with a multitude of different and partly contrary challenges. Higher demands on passive safety tend to result in weight increase while ecological aspects like reduction of fuel consumption and carbon dioxide emission call for light weight constructions. The application of high strength steels was a first answer to ensure the required safety directives in a light weight car body construction. Although high strength steel has superior mechanical properties, stamping operations become more difficult. High strength goes parallel with reduced formability, increased spring back behavior and excessive tool wear in cold forming application.^[1,2]

Press hardening is an effective technique to fulfill the contradicting requirements of very high strength levels (>1500 MPa) in combination with a high complexity of

geometry. Hardenable boron steel (between 0.002 and 0.005 wt% boron) is austenitized at a temperature of >850°C and then quenched between cold tools with cooling rates greater than 25 K s^{-1} to attain martensitic transformation. The utilization of hardenable steel in combination with press hardening applications began in the 1990s and is mainly used for producing passive safety components such as side impact beams, bumper beams, and different types of reinforcement components.

Besides passive safety and weight reduction, corrosion protection is another major aspect for materials in automotive industry. Systems of particular interest are those who are able to act as a sacrificial anode for the base material for example like the zinc coating of galvanized steel. The use of continuous galvanized steel sheet as feedstock material for press hardening leads to components of very high strength levels with cathodic corrosion protection.

Generally heat treatment of galvanized steel sheet causes besides surface oxidation, chemical interdiffusion of zinc within the steel substrate. The Zn–Fe system was investigated since the beginning of 20th century and has been subject of a number of reviewed papers.^[3–5] One of the most widely accepted Zn–Fe equilibrium phase diagram is that of Burton and Perrot.^[5] Burton and Perrot describe the system Zn–Fe consisting of liquid phase, several Zn–Fe phases named Γ_1 -, Γ_2 -, δ -, ζ -phase, as well as

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mixed crystals of α - and γ -Fe. A good description of each Fe–Zn intermetallic phase as well as reactions during galvannealing is found in Ref.^[6]

Besides intermetallic phase transformation also surface oxidation occurs during the press hardening process when performed at ambient atmosphere. High temperature oxidation of metallic materials is an oxidation reaction resulting in the conversion of metals in oxides when exposed to high temperatures in the presence of oxygen. Oxide layers are formed dependent on the chemical composition of the metal, respectively, the alloy. These oxide layers can prevent the metal from further attack by oxygen forming a diffusion barrier. In the case of oxidation of a number of alloys the scale may consist of double layers. The outer oxide layer of the scale is monophase and consists of the oxidized base metal, whereas the inner layer is a heterophase mixture of the oxidized base metal and oxidized alloying components. This kind of inner oxidation is typical for alloys where both compounds form oxides and the alloying element has higher oxygen affinity than the base material.^[7,8]

The annealing temperatures for galvannealing are usual in a range of about 550°C.^[6] Annealing as a part of press hardening process is done by much higher temperatures and faster heating up rates. The importance of press hardening and its application on galvanized steel sheet to generate coatings with cathodic corrosion protection, underlines the importance of the research in this area.

This paper focuses on surface oxidation, coating formation, and corrosion characteristics of press hardened hot dipped galvanized steel sheet with an original zinc coating of 70 g m⁻² and an oven temperature of 900°C.

Several works on this topic exist,^[9–11] varying in coating type and annealing conditions. Studies exist concerning the interactions and phase evolutions between coating and steel sheets for hot dip Al–Si coatings in Ref.,^[10] Zi–Ni coatings in Ref.^[11], and also for hot dipped galvanized coatings which much higher coating weight in Ref.^[11] Due to the fact that coating formation during press hardening is of course influenced by coating weight at the initial state, the present work cannot be combined with former work in Ref.^[9]

2. Materials and Methods

2.1. Materials

The material used for this study was supplied by voestalpine Stahl GmbH. Steel substrate was a common hardenable boron alloyed carbon manganese steel 22MnB5 with a blank thickness of 1.5 mm. The main alloying components were 0.22 wt% C, 0.25 wt% Si, 1.2 wt% Mn, 0.32 wt% Cr, and 30 ppm B. The samples used for this study were hot-dipped galvanized steel sheet with a conventional zinc coating (Z) consisting of Zn with 0.5 wt% Al, produced on a large

scale plant. The average coating weight per side was 70 g m⁻², corresponding to a coating thickness of 10 μ m. Rectangular samples with dimensions 150 mm \times 100 mm were machined cut out of industrially produced coated steel.

2.2. Thermal Treatment

Heat treatment was done in a 12 kW Nabertherm L20/14-S1 radiation furnace. The furnace was preheated at 910°C and all experiments were performed at ambient atmosphere.

All samples were oiled with PL3802-39S and annealed for 6 min at a furnace temperature of 910°C before hardening between cold steel plates.

To describe surface oxidation and coating formation specimens were heated in a temperature range of 400–900°C in steps of 50°C without soaking before quenching in water, respectively, between cold steel plates to generate flat samples. All experiments showed that surface and coating were identical for samples hardened in water and between cold steel plates. Temperature was controlled by a K-type thermocouple DIN IEC 584 contacted to the substrate by spot welding.

2.3. Corrosion Test

The samples were exposed to cyclic corrosion tests VDA 621-415 further mentioned VDA. This test was performed automatically in a Weiss SC 1000 chamber. Details on weekly cycle of the VDA test are presented in Figure 1.

2.4. Characterization

Samples were taken from the center of the test panels near the thermocouple contacts. Cross-sections were prepared

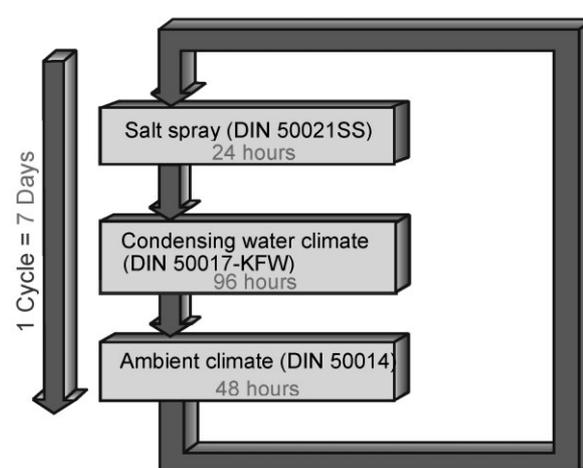


Figure 1. One week cycle of VDA 621-415 corrosion test.

and examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray fluorescence analysis (EDX). SEM investigations of the cross-section were carried out by using the back-scattered electron mode to emphasize the different metallic phases. The investigation of the corrosion characteristics was done by electrochemistry and microscopically inspection. For corrosion experiments all samples were surface conditioned by CO₂ blasting to eliminate the influence of oxides in corrosion.

For SEM and EDX investigations a Zeiss Supra 35 scanning electron microscope combined with an EDAX LEO 1530 was used.

Electrochemistry was done with a Princeton Potentiostat/Galvanostat – Model 263A. The electrolyte consists of 100 g l⁻¹ ZnSO₄ · 7H₂O and 200 g l⁻¹ NaCl. Temperature was 25 °C, the electrolyte was aerated and the reference electrode was an Ag/AgCl electrode in 3 mol l⁻¹ KCl. XRD analyses were done with a X'Pert Pro MPD from Panalytical with a Co-Anode.

3. Results and Discussion

3.1. Intermetallic Phase Formation During Heat Treatment

Figure 2 illustrates changes in microstructure of the coatings during thermal treatment. Element concentration was measured by EDX while chemical composition was analyzed by XRD (Figure 3).

The use of the back-scattered electron detector leads to different shades of gray for different metallic phases. Zinc rich phases are represented brighter than iron rich phases due to the fact that heavier elements have a better electron reflection than lightweights.

The formation of intermetallic compounds on galvanized steel sheets during heating up initiates after the melting of the zinc coating. The liquid zinc coating dissolves iron and zinc-iron reactions starts beginning from the steel substrate forming several Fe-Zn phases.

The first compound, formed at the zinc-iron interface with an iron content of 10 wt% was identified in the sample

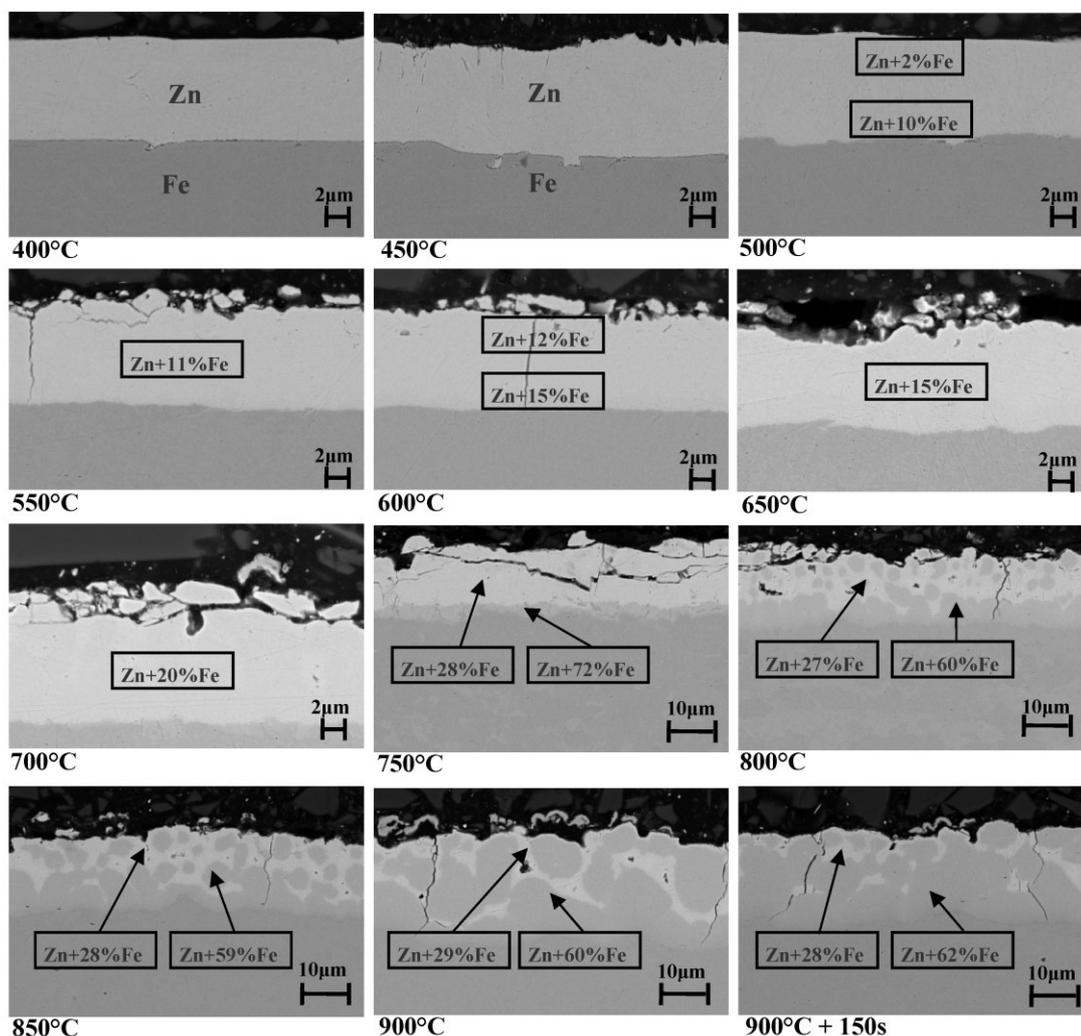


Figure 2. Cross cut SEM micrograph of galvanized steel after annealing at defined temperatures; Element concentration in wt%.

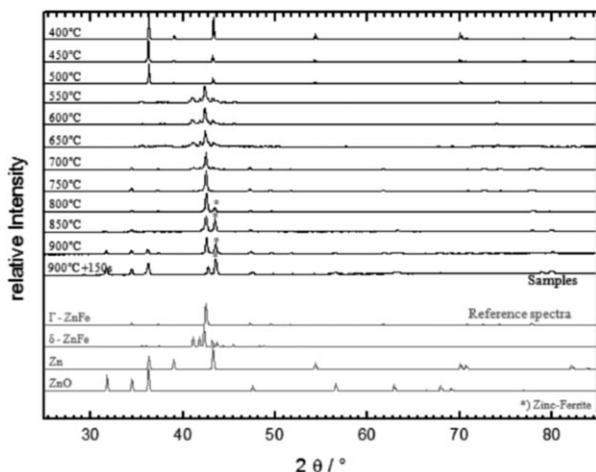


Figure 3. XRD spectra of galvanized steel sheet, annealed at defined temperatures. 400°C for the upset spectra.

annealed at 500°C. In the coating, there is still some iron containing zinc melt, so the conversion of the coating is not completed reaching this temperature. Further annealing up to 550°C results in a complete transformation into a coating with an iron content of 11 wt%, which corresponds to the δ -Zn-Fe phase in Ref.^[5] XRD measurements (Figure 3) prove this transformation from Zn into δ -Zn-Fe phase between the melting point of Zn (420°C) and 550°C.

At 600°C a continuous conversion from δ -Zn-Fe phase into Γ -Zn-Fe phase (short Γ -Zn-Fe phase) occurs, starting again from the steel-coating interface. XRD measurements show that the transformation into Γ -Zn-Fe phase is at 700°C nearly completed. Former annealing leads to an increase of iron concentration in the coating as a result of continuous iron diffusion. These results almost coincide with the results in Ref.^[6] Marder observed that δ -Zn-Fe phase layer is no longer stable at 665°C and Γ -Zn-Fe phase forms.

At 750°C the iron content is about 28%, which is corresponding to the Zn-Fe equilibrium phase diagram in Ref.^[5] the maximum iron concentration for the Γ -Zn-Fe phase. At the steel coating interface a dark area forms with an iron concentration of 72% corresponding to a zinc saturated α -Fe (zinc-ferrite). These circumstances indicate that the next phase transformation from Γ -Zn-Fe phase into zinc-ferrite occurs, starting at about 750°C. Further annealing up to a process temperature of about 900°C results in more conversion into zinc-ferrite. Examination of XRD measurements show first signals of zinc-ferrite at 800°C, getting more intense with higher temperature, which corresponds to cross section analyses (considering with the information depth of XRD).

According to the Zn-Fe equilibrium phase diagram in Ref.^[5] several Zn-Fe phases were detected above their stability zone. The δ -Zn-Fe phase should only be stable up to 672°C and the Γ -Zn-Fe phase up to 782°C. As

described above the δ -Zn-Fe phase has been detected until 700°C and the Γ -Zn-Fe phase actually at 900°C even if held for several minutes.

The reason for this is an incomplete phase transformation caused by too fast heating-up rates (4–7 K s⁻¹) so the thermodynamic equilibrium cannot be achieved.

3.2. Surface Oxidation of Press Hardened Galvanized Steel Sheet

Figure 4 shows the surface changes of hot dipped galvanized steel sheet during thermal treatment as part of press hardening process.

At the initial state the coating consists of a homogeneous layer of zinc with some dissolved Al (\approx 0.5 wt%) which was added to the coating bath. Aluminum on the one hand is added to form a thin inhibition layer of a Fe-Al-Zn intermetallic compound avoiding Zn-Fe reactions during coating process. On the other hand aluminum forms a thin continuous Al₂O₃ layer on the surface that inhibits further oxidation by acting as a passive layer.^[6]

After liquefaction of the Zn coating, the thin inhibition layer dissolves and Al diffuses to the surface based on the oxophilicity of aluminum and a concentration gradient caused by continuous aluminum oxidation on the surface. This oxide layer prevents from further oxidation acting as a protective layer. At 550°C the formally protecting Al₂O₃ layer features several damages, as result of intermetallic phase formation. This leads to the formation of zinc oxides when reaching the required temperature and oxygen partial pressure. At 700°C the transformation from δ -Zn-Fe phase into Γ -Zn-Fe phase occurs causing another fragmentation of the Al₂O₃ layer. Several small zinc oxide

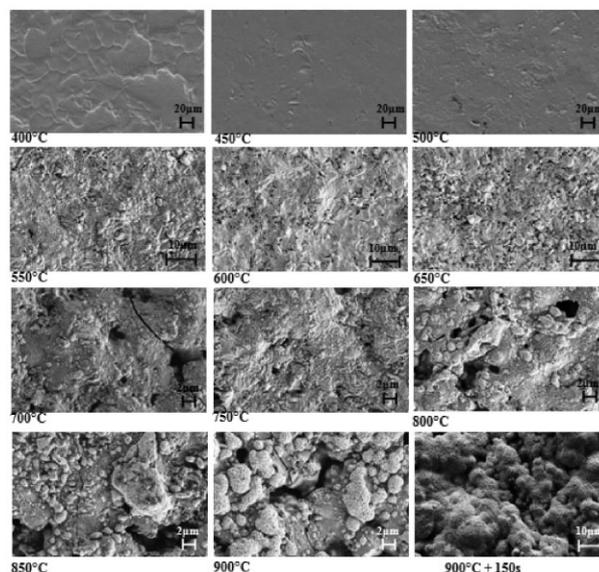


Figure 4. SEM micrograph of the surface of galvanized steel after annealing at defined temperatures.

islands appear, grow together leading to a compact closed oxide layer which prevents further oxidation by acting as a diffusion limiter. Composition and morphology of this generated oxide layer is discussed in the next chapter.

3.3. Surface and Microstructure of Galvanized Steel Sheet after Annealing

During austenitisation a significant change in the coating occurs as described above. The formally $10\ \mu\text{m}$ thick zinc coating changes into an about $20\ \mu\text{m}$ thick coating consisting of zinc saturated α -iron and Γ -Zn-Fe phase regions. **Figure 5** shows the SEM image of a sample cross-section from press hardened galvanized steel sheet. The light areas represent Γ -Zn-Fe phase and dark areas zinc-ferrite. The martensitic steel substrate can be identified as separated darker area under the coating.

After press hardening the surface is covered with an oxide layer almost consisting of ZnO. **Figure 6** illustrates surface images combined with EDX analysis and **Figure 7** shows TEM images of cross sections prepared by FIB.

The oxide layer is between 1 and $2\ \mu\text{m}$ thick, consists of successively arranged layers of Al_2O_3 and ZnO, containing also further oxidized steel alloying elements namely Mn and Cr. The upper oxide layer is composed of ZnO with some Mn containing regions which can be identified in **Figure 5** as darker area in the oxide layer and in **Figure 6** as MP1 where the oxide layer seems to be bit

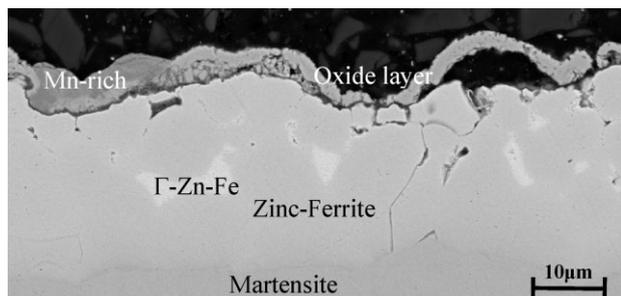


Figure 5. Cross cut SEM micrograph of press hardened galvanized steel sheet.

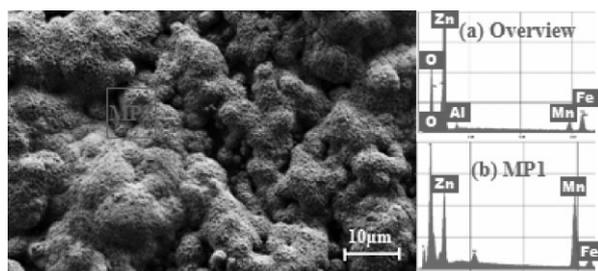


Figure 6. SEM micrograph of the surface of press hardened galvanized steel sheet.

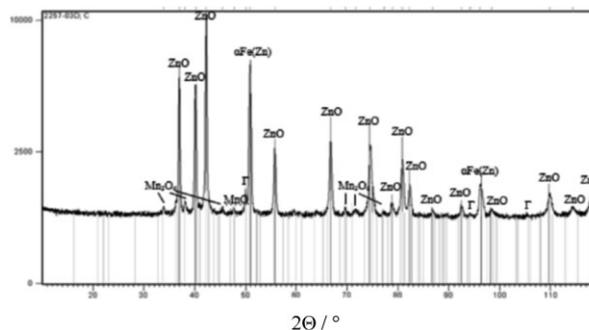


Figure 7. Low angle XRD of press hardened galvanized steel sheet.

more plane. A low angle XRD in **Figure 7** identifies the oxides as ZnO, Manganese(II)oxide, and the spinel type oxide hausmannite ($\text{MnO} \cdot \text{Mn}_2\text{O}_3$).

The lower oxide layer is composed of the fragmented Al_2O_3 layer and a mixture of the oxidized components Al, Cr, and Zn (see **Figure 8**). During surface oxidation Al_2O_3 fragments from the formally thin Al_2O_3 layer are covered with the upper oxide layer. A heterophase mixture of Al, Cr, and Zn oxides is a result of inner oxidation.^[7,8]

3.4. Corrosion Behavior of Press Hardened Galvanized Steel

Figure 9 shows a galvanostatic measurement of galvanized steel before and after press hardening at a current density of $11.76\ \text{mA cm}^{-2}$. The potentials for the Γ -Zn-Fe phase with $-0.54\ \text{V SHE}$ and for zinc-ferrite with $-0.4\ \text{V SHE}$ are significantly lower than the steel potential of $-0.22\ \text{V SHE}$ which indicates that the generated coating offers cathodic

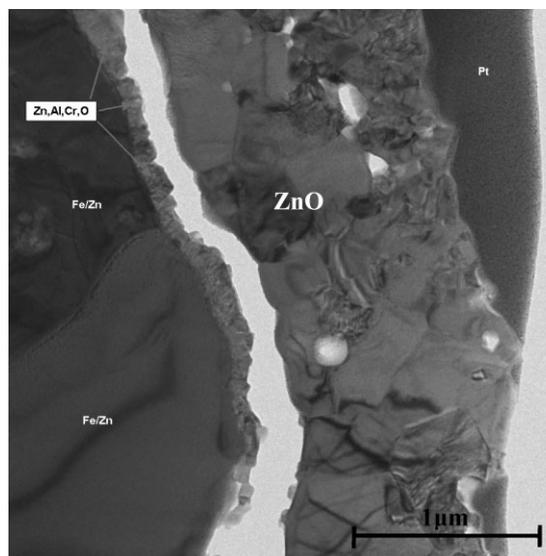


Figure 8. Press hardened galvanized steel sheet – TEM image of cross-cut prepared by FIB.

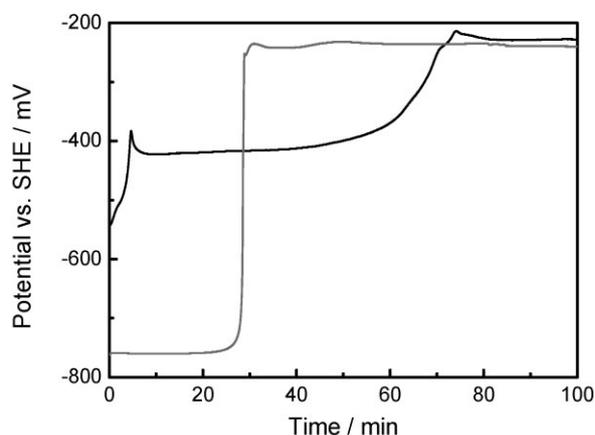


Figure 9. Galvanostatic measurement of galvanized steel before (red line) and after press hardening (black line) versus SHE. Electrolyte: $100 \text{ g l}^{-1} \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O} + 200 \text{ g l}^{-1} \text{ NaCl}$; $T = 25^\circ\text{C}$; aerated; $I = 11.76 \text{ mA cm}^{-2}$.

corrosion protection for the substrate. The dissolution time of the coating for press hardened samples is more than twice, which can be explained by higher coating thickness and reduced corrosion rate caused by lower potential differences. The overshooting potential after 2 min dissolution in the hardened sample remains unexplained.

Important information about the corrosion behavior is also given by cross-sections analysis of the corroded specimens in VDA 621-415 shown in **Figure 10**. Press hardened galvanized steel sheet shows red corrosion products right from the beginning of exposure. Therefore the determination of base material attack is only possible by the means of cross-cuts.

It is shown that the generated coating offers protection for the steel substrate. After 10 weeks VDA 621-415 no base material attack can be observed in comparison to unhardened samples which show base material attack after 2 weeks in VDA 621-415. Galvanized steel sheet after press hardening shows more than 5 times longer protection for base material attack in VDA 621-415. An explanation for this is the higher coating thickness caused by press hardening process and lower corrosion rate.

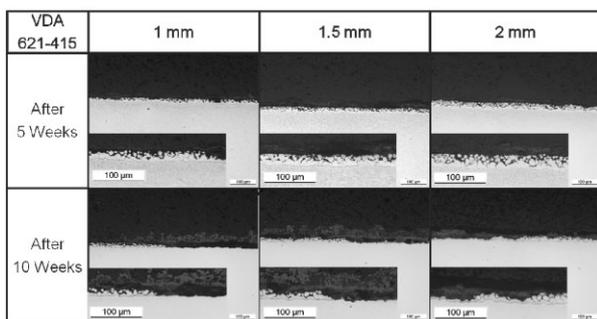


Figure 10. Cross-Cut SEM micrograph of press hardened galvanized steel sheet after 5 and 10 weeks in VDA 621-415.

All in all hot dipped galvanized steel sheet has a much higher corrosion resistance after press hardening and the generated coating is still able to offer protection for the steel substrate according to the cathodic protection effect, which is also observed in Ref.^[12]

4. Conclusion

Austenisation of galvanized steel sheet causes a significant change in coating formation. The formally $10 \mu\text{m}$ thick zinc coating changes during thermal treatment crossing several Zn-Fe phases into a $\approx 20 \mu\text{m}$ thick layer, consisting of zinc saturated α -iron and Γ -Zn-Fe phase regions. Galvanostatic measurements and cross section analysis prove that this generated coating shows more than 5 times longer corrosion protection for the steel substrate according to the cathodic protection effect. Higher corrosion resistance is caused by higher coating thickness as well as reduced corrosion rate.

Surface changes caused by intermetallic phase formation causes a fragmentation of the Al_2O_3 protecting layer of galvanized steel sheet, which leads to surface oxidation. After press hardening the surface is covered with a $1\text{--}2 \mu\text{m}$ thick oxide layer consisting of successively arranged layers of Al_2O_3 and ZnO , containing also further oxidized steel alloying elements namely Mn and Cr. Mn is found in the upper oxide layer as manganese(II)oxide and the spinel type oxide hausmannite ($\text{MnO} \cdot \text{Mn}_2\text{O}_3$), while Cr is located in the lower layer.

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