Contents lists available at ScienceDirect





Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effects of alloying elements on surface oxides of hot-dip galvanized press hardened steel



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ARTICLE INFO

Keywords: Press hardening Metal coatings Oxide formation Auger electron spectroscopy Secondary ion mass spectrometry Transmission electron microscopy

ABSTRACT

The effects of steel alloying elements on the formation of the surface oxide layer of hot–dip galvanized press hardened steel after austenitization annealing were examined with various advanced microscopy and spectroscopy techniques. The main oxides on top of the original thin Al_2O_3 layer, originating from the primary galvanizing process, were identified as ZnO and $(Mn,Zn)Mn_2O_4$ spinel. For some of the investigated steel alloys, an additional non–uniform, several nanometer thick Cr enriched film was found at the Al_2O_3 layer. At a sufficiently high concentration, Cr can act as a substitute for Al during annealing, strengthening and regenerating the original Al_2O_3 layer with Cr_2O_3 . Further analysis with secondary ion mass spectrometry allowed a reliable distinction between ZnO and Zn(OH)₂.

1. Introduction

In recent years, lightweight ultra–high strength steels (UHSS) have become one of the most sophisticated materials for automotive applications such as chassis components. With challenges such as emission reduction, stringent safety requirements and the new focus on e–mobility, ever–lighter construction of structural car body parts is essential for low–cost and high–value manufacturing. Hot–dip galvanized press hardened steel (PHS) is a widely used variant with excellent galvanic corrosion resistance, while maintaining the mechanical capabilities of hot–formed UHSS [1,2].

Generally, several metal based coatings are used for PHS applications, containing Al, Zn, Ni or Mg that provide different advantages and disadvantages [3]. For instance, Al–Si based coatings exhibit excellent resistance to corrosion. However, intermixing of the ferrite stabilizer Al with the base steel during welding can lead to drastic effects on the tensile properties during press hardening, which makes them less desirable for structural car body parts. Therefore, Zn–based coatings are a promising alternative due to their cost effectiveness, corrosion properties and weldability [4–6]. Typically used are continuously hot–dip galvanized (GI) Zn coatings with low Al additions (< 0.5 wt%) or galvannealed (GA) Zn–Fe coatings with even less Al (< 0.16 wt%) added to the Zn bath. During hot–dipping in the liquid Zn bath, Al reacts with Fe from the steel strip surface and forms a Fe₂Al₅ inhibition layer. In Zn coatings, this layer prevents interdiffusion of Fe and alloying elements from the steel and the Zn coating. However, in GA coatings the lower amount of Al in the Zn–bath prohibits the formation of an inhibition layer during inductive heat treatment [7] and during the galvannealing process, interdiffusion of Zn and Fe results in a coating with 8–12 wt% Fe [8].

For a better understanding of the wetting behavior during galvanization, the role of oxidized alloying elements on the uncoated steel surface were investigated by Sagl et al. [9,10] and found to be a major factor on the general galvanizability of the steel strips. In further investigations by Arndt et al. [11], the huge influence of pre–oxidized alloying elements (mainly Mn) on the wetting behavior could be confirmed and a detailed model for the wetting process was proposed.

A detailed overview of the coating evolution during annealing was given by Kang et al. [12] and Järvinen et al. [13,14]. Microstructure analysis of Zn and Zn–Fe coatings at the steel–coating interface region

https://doi.org/10.1016/j.surfcoat.2020.126466

Received 1 July 2020; Received in revised form 25 September 2020; Accepted 28 September 2020 Available online 03 October 2020 0257-8972/ © 2020 The Authors. Published by Elsevier B.V. This is an open access article under the 0

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for different manganese–boron steel grades showed that higher C contents, as well as higher contents of the alloying elements Mn and Cr resulted in more stable γ –Fe(Zn). However, the evolution of the surface oxide region was not considered. The effects of surface oxides on the steel strip before galvanization were investigated by Chen et al. [15], comparing standard GI coatings with GA coatings on dual phase steels. In further studies, the diffusion process for the Fe–Zn phases depending on the Zn concentration in GA coated 22MnB5 was described by Wang et al. [16].

A brief overview of the post–annealed coating surface of GI coated PHS was given by Autengruber et al. [17], where a mixture of mainly ZnO and Mn_3O_4 was found on top of a thin Al_2O_3 layer. The Al_2O_3 layer was shown as a consequence of low Al additions in the Zn bath during galvanization acting as a barrier, which prevents oxidation of the liquid Zn immediately after hot–dipping [7]. Based on these findings, heating experiments were performed by Lee et al. [18] describing the sequence of the oxide formation due to the temperature change during annealing. Furthermore, low heating rates correlated with a higher fracturing of the initial Al_2O_3 layer and thus with increased ZnO formation. A thorough description of the microstructure evolution during austenitization, as well as the oxidation and corrosion behavior of 5 wt% Al–Zn coated steel was presented by Chang et al. [19,20].

The results of these works indicate a strong influence of the alloying elements on the final coating structure and especially on the oxide formation. The quality of post–annealing processing techniques like resistance spot welding, adhesive bonding, painting or application of further (organic) coatings are influenced by the oxides on the surface of the coated steel. Therefore, the uppermost oxide layer after press hardening austenitization annealing of four industrial steel grades commonly used in PHS applications were investigated.

First differences in the structural and optical appearance of the surfaces were shown on a mm to µm scale by optical light microscopy (OLM). A noticeable characteristic was the different visual appearance of the surface for GI and GA coated specimen. Due to the limited resolution of OLM, further measurements with techniques using a higher lateral resolution were necessary. By means of scanning electron microscopy (SEM) combined with additional detection techniques like energy dispersive X-ray spectroscopy (EDX) and Auger electron spectroscopy (AES) the prepared cross sections were investigated on a scale ranging from several µm down to sub µm. A detailed overview of the phase mixture and microstructure of the coatings could be determined. Additional chemical investigations were made by time-of-flight secondary ion mass spectrometry (ToF-SIMS) powered by a helium ion microscope (HIM). Small features with only a few nanometers in diameter were found. Thus, further investigation required the sub--nanometer resolution of a transmission electron microscope (TEM). A thorough crystallographic analysis with selected area diffraction (SAD) was performed. EDX measurements in scanning mode (STEM) allowed for a reliable description of the different oxide phases in the coating.

2. Material and methods

2.1. Material and sample preparation

The elemental compositions of the investigated steel substrates are given in Table 1. The basic steel grades are manganese–boron steels

with slight differences in alloy compositions. The exception is the steel HX340LAD, which is, compared to the other specimens, a boron free material with less C and Mn. The 22MnB5 contains a maximum amount of 2 wt% Mn as well as 0.5 wt% Cr. 20MnB8 and 22MnCrB8–2 have a slightly higher amount of Mn compared to the 22MnB5, while only the 22MnCrB8–2 contains also the same amount of Cr as part of the desired alloy composition. In addition to the chemical differences of these steel grades, the Zn–coating types were varied. HX340LAD and 22MnB5 received a standard GI coating, while 20MnB8 and 22MnCrB8–2 were GA coated.

In industrial applications, a continuously hot–dip galvanizing process includes a strip surface cleaning step and an austenitization step at temperatures from 700 to 850 °C in a radiant tube furnace under HNX atmosphere. During the heat treatment, selective oxidation within the steel matrix occurs, which defines the wettability of the steel strip surface. After hot–dipping in the liquid Zn bath at about 450 °C, excess Zn is removed by gas knifes. If the coating received the additional galvannealing heat treatment, the coated steel strip enters the induction furnace right after hot–dipping and wiping. The desired temperature of about 500 °C is reached within seconds, which allows the transformation of a pure Zn coating to a Zn–Fe coating with 8 to 12 wt% Fe. Subsequently, the galvanized steel strip is cooled for a complete solidification.

In this work, sheets in the A4 format (297 \times 210 mm²) were cut with a metal sheet cutting machine from the industrially produced steel strips and austenitization annealed in a Nabertherm N41/H lab oven in ambient atmosphere with a final annealing temperature of 910 °C (see Fig. 1) to simulate the industrial process. Two annealing series have been fabricated, one with a 45 s holding time and another with a 200 s holding time after reaching a temperature of 870 °C. The heating rates, which are determined via a heat couple attached to the surface of the specimen, for the GI and GA coated specimens vastly differ due to the compositions and heat absorption capabilities. The GI coated specimens (blue lines in Fig. 1a,b) had a rather constant heating rate of 5 $^{\circ}$ C s⁻¹ up to about 550 °C, with a quick rise to 670 °C with 7 °C s⁻¹. The GA coated specimens (red lines in Fig. 1a,b) had a very high initial heating rate of up to 15 $^\circ\!C~s^{-1}\!,$ which declined rapidly after reaching 670 $^\circ\!C$ and showed similar heating rates as the GI coated specimen above 670 °C.

The heat treatment resulted in a phase–evolution of the Fe–Zn binary system as described by Marder [7,21] and Janik et al. [8]. Above 550 °C, the emissivity of the surface increases due to the replacement of liquid Zn with δ –phase crystals. At 670 °C the phase mixture contains Γ –phase and liquid Zn, resulting in lower overall emissivity and thus lower heating rate. After the heat treatment, samples were quenched in ambient air, with cooling rates above 20 °C s⁻¹.

Small strips with 8 mm width were cut from the hardened steel plates with a guillotine shear and further cut into pieces with a dimension of (8 \times 5) mm² by a Struers Accutom–100. To ensure, no thermal changes were induced through the cutting process, watercooling was used to reduce the sample heating. Before each measurement, each specimen was cleaned in an ultrasonic bath in various solvents (ethanol, 99.9%; acetone 99.9%; isopropanol 99.9%; tetrahydrofuran 99.9%) to remove surface contaminations resulting from the production process and sample handling. This is especially necessary for AES investigations due to the very high surface sensitivity, as

Table 1

Alloy contents of the different steel grades in weight percent. All specimen have a sheet thickness of 1.5 mm with coating on both sides.

Steel grade	Coating weight side/side in g/m^2	С	Si max	Mn max	Al	Cr max	Ti + Nb max	В
HX340LAD	GI 70/70	$\leq 0,11$	0,5	1,4	\geq 0,015	0,05	0,10	-
22MnB5	GI 70/70	0,20-0,25	0,5	2,0	0,02-0,10	0,50	0,05	0,002-0,005
20MnB8	GA 90/90	0,17-0,23	0,5	2,5	0,02-0,30	0,05	0,05	0,002-0,005
22MnCrB8–2	GA 90/90	0,20-0,25	0,5	2,5	0,02-0,30	0,50	0,05	0,002-0,005



Fig. 1. Temperature curves measured with thermocouples during annealing in a lab oven for GI and GA coated specimens (a) and their corresponding heating rates (b).

similar investigations on ZnMgAl coated specimen have shown [22].

Sample preparation of focused ion beam (FIB)–thinned TEM lamellas is a challenging process due to the complex morphological structure and heterogeneous phase mixture of the coating. After austenitization heat treatment, large cavities underneath the porous and sometimes loose oxide layer had a negative influence on the stability of the lamellas during FIB thinning. These cavities are susceptible to milling artifacts, which lead to non–uniformly thinned TEM–specimens [23]. Moreover, redeposition of the sputtered material onto the lamellas were found to be increased along these holes, creating artificial material mixtures, which may cover interesting features of the coating structure.

The best working solution was an application of the two-component, solvent-thinned epoxy-phenolic adhesive M-Bond 610 from Vishay Micro-Measurements, which is typically used for conventional TEM-sample preparation. After the described cleaning process, a small droplet of the liquid adhesive with at least 2 mm diameter was applied on the surface. The droplet size determines the quality of the cavity filling, as it must provide enough volume to reliably reach deeper holes within the coating. Afterwards, the adhesive was cured at room temperature in a vacuum chamber for 48 h. The adhesive was pulled into the holes through cracks and channels in the coating due to the vacuum and capillary effects.

An exemplary sample is shown in Fig. 2. Here, the cavities filled with the adhesive (A) are located between the intermetallic Fe–Zn phases (B) and the oxide layer (C). On top of the oxide, a partially remaining platinum layer (D) from the FIB–milling process is visible. The now hardened epoxy adhesive mechanically supports the porous, fragile oxide layer. Moreover, redeposition at the edges of the cavities is prevented during FIB milling and no increased curtaining around the holes was found.

Cross sections for SEM and HIM investigations were prepared by manual mechanical grinding with SiC grinding paper and polishing with diamond paste with a grain size down to 1 μ m. The final polishing post–cleaning was done by Ar⁺ sputtering in a Leica EM TIC 3X with 8 kV accelerating voltage at -100 °C. The sputtering process at cryogenic temperatures with three converging aligned ion guns reliably



Fig. 2. STEM–BF image of a finished TEM–lamella where adhesive (A) was used to fill the pores, Fe–Zn intermetallic phases (B), oxide layer (C) and partially removed platinum cover (D).

produced a smooth, hardly damaged surface for AES, EDX and SIMS measurements. In order to protect the coating from redeposition during Ar^+ sputtering a protective layer is necessary. For this purpose, either the epoxy adhesive was sufficient or an additional ink layer from a black felt tip pen was applied. The prior application of the epoxy adhesive proved to be superior to the black pen, as it smoothened the cracks and cavities in the cross sections, resulting in almost no curtaining effects from the Ar^+ sputtering.

2.2. Analytical methods

In the scope of this work, several electron and field ion microscopes have been utilized. A Zeiss Supra 35 was used for EDX investigations with an $X-Max^N \ 80mm^2$ detector from Oxford instruments on cross section polished (CSP) specimen.

Auger electron measurements were performed in an ultra-high vacuum Jeol JAMP 9500F field emission electron microscope. The Auger microprobe uses a hemispheric analyzer, which provides a spectral range from 0 to 2500 eV. The instrument was operated with a primary electron energy of 30 keV and currents of 10 to 20 nA and supports recording of scanning Auger elemental mappings in constant analyzer energy mode. Additionally, an Ar^+ ion gun was available for sputtering of the specimen surface with ion energies of 0.2 to 3 keV. Elemental mappings were recorded according to the atomic number, starting with C, followed by O and the other elements. This procedure ensured reliable C and O mappings, due to higher C contamination with increasing measurement duration.

A Zeiss 1540XB CrossBeam was used for imaging of the original sample surfaces. Additionally, the FIB column of the Zeiss 1540XB was used for TEM sample preparation, where an accelerating voltage of 30 kV with milling currents from 100 pA to 20 nA, were used for imaging and sample milling of the investigated specimen.

TEM measurements were performed on a Jeol JEM–2200FS, where a Schottky field emission gun was operated at 200 kV acceleration voltage. The microscope can be operated either in standard TEM or in STEM mode. In STEM mode, a bright field (BF) detector as well as a high angle annular dark field (HAADF) detector were used. Attached to the microscope column is a silicon drift detector X–Max^N 80 T from Oxford Instruments for nanoscale EDX investigations. For all EDX experiments with the various microscopes, the software AZtec from Oxford Instruments was used.

The helium ion microscope (HIM) Orion NanoFab by Zeiss, was operated at 30 keV with neon as primary ion source and extended with a custom designed ToF–SIMS setup [24]. The high brightness of the ion source can reach up to 10^9 A cm⁻² sr⁻¹ and allows for a lateral resolution for sputtering of 1.8 nm. The samples were biased at \pm 500 V



Fig. 3. SEM image and EDX mappings of a CSP 22MnCrB8–2 + GA (45 s > 870 °C) sample; (a) SE image; (b,c) EDX mappings with 5 keV primary electron energy. The layered structure shows two distinctive Fe–Zn intermetallic phases (1), which are separated from the Mn–Zn–rich oxide by a thin Al₂O₃ layer (2). Within the Zn–rich–phase, small particles of Al and Si oxide can be found (3).

in order to select either positive or negative ions for the ion spectrometer [24,25].

3. Results

3.1. Chemical compositions

Detailed investigations with SEM–EDX were made on CSP samples with the pre–applied adhesive stabilization (see Fig. 3). The secondary electron (SE) image depicted in Fig. 3a already shows a complex multi–phase structure according to the different gray values arising from Z–contrast. The element distributions of C, O, Mn, Fe and Zn in Fig. 3b, show at least two different Fe–Zn intermetallic phases (α –Fe(Zn) and Γ –phase, 1) as well as Zn– and Mn–rich oxides in the top region. In the mapping showing the remaining alloying elements (see Fig. 3c), a thin and slightly fractured Al₂O₃ layer could be identified (2) in between the oxide and Fe–Zn phases. Alongside the Al₂O₃ layer, small particles of SiO₂ were found (3). In the top right corner, above the porous oxide layer, the applied epoxy adhesive is detectable as it consists mainly of C.

In order to achieve a sufficiently high lateral resolution to reliably locate the small Al_2O_3 particles of the layer, a primary electron energy of 5 keV was used. A downside of the low excitation energy is the restricted spectral response, limiting the detectable spectral lines to low energy X–rays. This constraint affected the measurement adversely while monitoring Cr combined with O, as the Cr L α line is overshadowed by the strong O K α line. Therefore, the Cr signal cannot be separated from the O signal and the measured Cr distribution is related to O.

Complementary to the SEM–EDX measurements, scanning AES was utilized for elemental mappings of cross sections. A major advantage of AES over EDX is the low information depth and interaction volume as well as a high lateral resolution. However, the high surface sensitivity requires special care while cleaning the samples. The prior application of the epoxy adhesive resulted in an ever–increasing surface carbon layer during measurements due to electron beam induced deposition and surface diffusion processes.

Fig. 4 shows mappings on the interface between oxide and Zn–Fe coating. Similar to the SEM–EDX measurement, the SE image depicts various phases, distinguishable by their respective gray values in the image. In the center of the images, higher concentrations of C, O and Al are present in the Fe–Zn phases indicating residuals from the partially fractured, primary Al_2O_3 layer. This layer separates the oxide and intermetallic Fe–Zn phases and on a closer look, it was identified as missing intensity in the Zn mapping. Similar to the previously shown SEM–EDX mappings (see Fig. 3), the top oxide layer consists of a Mn–rich oxide phase, which is enclosed in a Zn–rich oxide. Fe and Zn mappings allowed a clear distinction between the Fe–rich α –Fe(Zn) and the Zn–rich Γ –phase. The effect of carbon contamination can be seen in

the C-mapping. The top, oxide area has a strongly growing C layer, originating from the epoxy (out of view). Notable observations are the higher concentration of C on the α -Fe(Zn) phase at the bottom and on the small Al₂O₃ particles embedded in Γ -phase. This behavior presumably originates from a higher C contamination in the mentioned areas. The Al₂O₃ layer is highly fractured, lying in between oxide and Fe–Zn intermetallic phases. The C signal is more intense in the areas of the Al₂O₃ particles, caused by surface diffusion from the epoxy adhesive.

The same CSP specimen was further investigated with the Ne powered HIM. The results of a ToF–SIMS measurement depicted in Fig. 5 were recorded using a positive sample bias while the results shown in Fig. 6 were recorded with a negative bias. The mass to charge ratio was calibrated and calculated using known element peaks within the spectrum and assigning them to their respective elements like H, F and Al. The mapping allows a reasonable allocation of spectral peaks to most elements, isotopes and small molecules.

The SE image in Fig. 5a depicts the general structure of the coating layer on a larger scale. The epoxy adhesive shows up as dark regions on top of the specimen filling the cavity between the oxide layer and Fe–Zn phases. The oxide layer is visible as a distinct layer running from top left to middle right. In the bottom area, a single large α –Fe(Zn) grain is covered by Γ –phase. On the right–hand side, the oxide layer is attached to the Fe–Zn phases. The strongly varying gray values within the different structures are attributed to the different crystal orientations, leading to channeling and different SE yields in the HIM [26]. Diagonally running scratches visible in the center of the image are artifacts from the CSP process. However, due to the prior applied epoxy those scratches are not deep and thus negligible for the ToF–SIMS measurements.

In positive bias mode, metals have high relative sensitivity factors (RSF), as seen in the spectral response in Fig. 5d. Four peaks of the sum spectrum were selected, namely Al, Cr, Mn and Zn, and their respective elemental mappings are presented in Fig. 5b,c. Confirming the EDX and AES measurements, the uppermost oxide layer consists mainly of Zn with a distinct Mn enriched area embedded into Zn on the right. The Al_2O_3 film from the galvanization step is located on the bottom side of the ZnO layer. Additionally, Cr seems to accompany the Al_2O_3 layer and even expanding the thin oxide film, where the Al response declines. Both elements together form a continuous layer on the bottom side of the top Mn and Zn layer.

A closer look at the sum spectrum in Fig. 5d shows prominent peaks of various elements and molecules. A strong H peak was identified, followed by ¹²C with a much lower count rate. Similar to H, ¹²C is detected all over the investigated area and often accompanied by H to form various hydrocarbon molecules (C_xH_y). ¹⁹F with a similar low response as carbon could be detected, as there are no other isotopes with a similar mass–to–charge ratio. Beside the distinct peak of ²⁷Al, ⁵⁵Mn has the highest yield of the detected metals. Right before ⁵⁵Mn, a



Fig. 4. AES mapping on a cross section of a 22MnCrB8-2 + GA (200 s > 870 °C) sample. Shown are spectral intensity mappings of the most interesting elements. Darker colors correspond to higher intensity.

small peak of 52 Cr, which is almost overshadowed by the strong Mn peak is visible. The next prominent peak is 64 Zn before another peak appears at 71 u, which presumably originates from MnO.

A measurement on a negatively biased specimen is shown in Fig. 6. The layered structure is once more visible in the SE image in Fig. 6a. However, the overall image quality is comparatively low, due to the fast image acquisition procedure to avoid sample damage during imaging. For the highlighted area, the mappings of elemental O and of OH are depicted in Fig. 6b,c. O and OH are similarly distributed and can be found in the topmost layer of the coating. However, the mappings differ in the bottom region, where O shows a loose cluster of smaller particles in the left half, while OH is highly localized at the bottom right quarter.

The sum spectrum for the negatively biased measurement is displayed in Fig. 6d. Mostly non-metallic elements beginning with a prominent H peak could be identified. The next notable spectral peaks are related to ¹²C and slightly stronger CH, followed by almost equal ¹⁶O and OH peaks. A rather strong ¹⁹F peak is similarly distinctive as seen in Fig. 5d. Several peaks with higher mass-to-charge ratio are present, which cannot be clearly assigned. The strongest peaks may be C_2H (25 u) or ³⁵Cl and the small peak at 32 u could be related to O_2 .

The different yields of the detected elements are directly related to the RSF of said elements [27,28]. As RSF values are not yet available for He or Ne as primary ion sources, the measurements yield only qualitative information about the elemental composition of the investigated areas.

3.2. Nanoscale TEM analysis

As the results from SEM and HIM have shown, further investigations on a higher magnification are necessary to allow a better description of the oxide layer, in particular the finely structured interface between the Fe–Zn phases and the oxides. During FIB preparation of the lamella, the focus of the thinning process was to ensure a homogeneously thin electron transparent window at the interface region between oxide and intermetallic phases. The shape of the final TEM–lamellas was influenced by residual strain within the material (see Fig. 7). As the sample becomes thinner, tension is released leading to small bulging and a slight distortion of the thinned lamella. The bulged material is cut away and therefore, the lamella is thinner in this area, which is typically at the center.

As a result, the upper oxide layer is partially sputtered away and an increased curtaining effect can be observed as displayed in the micrograph in Fig. 7a. Different phases can be distinguished by the Z–contrast in the HAADF image. Within the oxide layer, two different materials can be identified. A thin separation layer can be observed between oxide and Fe–Zn phases. This layer is undamaged in the left half of the lamella, but appears to be fractured on the right half.

A more detailed view on the elemental composition was given by STEM–EDX analysis of the GA coated 45 s hardened 22MnCrB8–2 sample depicted in Fig. 7. The EDX mapping in Fig. 7b gives an overview of the elemental distributions in the sample. The oxide layer is divided in a large Mn–rich part and a Zn–rich part. The thin film of Al and Cr oxide acts as a separation layer to the subjacent Fe–Zn phases. The interface consists of an Al_2O_3 layer with less than 100 nm in thickness, where some parts are fractured and replaced by Cr_2O_3 .

A detailed EDX mapping with high magnification of the interface region in Fig. 7c gave an in-depth view of the oxide to Fe–Zn interface. The corresponding quantification of the sum spectra from the highlighted regions are shown in Table 2. The bottom Γ -phase (A) is separated from the upper oxides. Zn–rich (B) and Mn–rich (C) oxides sit on top of Al₂O₃ (D), which is accompanied by Cr₂O₃. Moreover, the Al₂O₃ layer is partially damaged in the left half of the recording and seems to be substituted by Cr₂O₃ (E). In order to improve the element quantification, the absorption correction of the EDX software was applied, which uses the additional parameters thickness and density for the calculations. However, the quantification of STEM–EDX is



Fig. 5. Positively biased ToF–SIMS measurements on a CSP and epoxy stabilized 22MnCrB8–2 + GA (200 s $\,>\,$ 870 °C) sample with SE image (a), elemental mappings of Al, Cr, Mn and Zn (b,c) and the sum spectrum of the measurement (d).

susceptible to wrong results for mixtures from various phases and thickness that strongly differ from used mean values. Nevertheless, the amount of oxygen on all highlighted areas is noticeable higher than expected for the investigated material. This behavior is common in STEM–EDX analysis, since oxides or hydroxides, which develop during sample handling on the cut lamella surfaces, contribute strongly to the signal due to the small interaction volume of thin TEM lamellas.

Measurements for the 200 s hardened HX340LAD specimen with GI coating are depicted in Fig. 8. The overall structure is similar to the 45 s hardened samples, with a few remarkable differences. The STEM—HAADF image in Fig. 8a shows the elemental distribution with different gray values. For example, the Mn–rich area within the oxide has a darker shade, compared to the dominant but brighter Zn area. The HAADF image also shows a thickness gradient in the thinned area indicating a thinning of the lamella from top to bottom and from left and right into the center. The large overview EDX mapping in Fig. 8b confirmed that the oxide layer consists of Mn and Zn oxides with grains of different sizes and orientations.

The EDX mapping also revealed a distinct layer of Al_2O_3 , which lies beneath the large oxide layer. It is visible that the layer is fractured and integrated partially into the Fe–Zn phase. The Fe–Zn phase escaped the Al_2O_3 layer at a fractured area on the left–hand side. Along with Al, an increased concentration of Cr is present at the interface. A very high magnification of the Al_2O_3 layer (see Fig. 8c) shows a faint Cr



Fig. 6. Negatively biased ToF–SIMS measurements on a CSP and epoxy enhanced 22MnCrB8–2 + GA (200 s > 870 °C) sample with SE image (a), elemental mappings of O (b) and OH (c) and the sum spectrum of the measurement (d). The horizontal streaks in (a) are a result from a fast recording procedure.

enrichment at the bottom side of the Al_2O_3 . Moreover, there is a small Nb–rich precipitate attached to the $(Al,Cr)_2O_3$ oxide layer.

For a better insight into the different elemental distributions of the involved phases, Table 3 shows different quantified areas as indicated in Fig. 8c. Similar to Table 2, the values for oxygen are overall too high. A Fe–Zn phase appears in (A) and Nb oxide is visible in (B), which is probably NbO₂ or Nb₂O₅ [29]. Cr and Al appear in the stable corundum structure as (Al,Cr)₂O₃ in (C) and (D) and Zn in (E) is native ZnO.

3.3. Crystallographic analysis

Fig. 9a shows a TEM–BF image of an investigated Mn–rich oxide grain with the used SAD aperture fitting the grain. The resulting SAD pattern is depicted in Fig. 9b where the best match of diffraction pattern simulations has been found for tetragonal $ZnMn_2O_4$ spinel in [5,0,2] direction, as the simulated pattern in Fig. 9c confirms. The quantified STEM–EDX spectra measured in the highlighted areas A and B match the found spinel structure, if an overestimated amount of O is taken into account. However, Autengruber et al. [17] found Mn_3O_4 on top of PHS instead of the measured $ZnMn_2O_4$. Both minerals have the same crystal structure (space group $I4_1/amd$) and similar lattice constants (see Table 4), making a clear identification difficult. Furthermore, depending on the ambient conditions during oxide–formation, Zn and Mn may interchange within the spinel crystal structure and form (Mn,Zn)



Fig. 7. TEM–lamella of 22MnCrB8–2 + GA (45 s > 870 °C) sample; (a) STEM–HAADF image reveals at least two phases in the oxide regime (top) separated by a thin layer from Fe–Zn intermetallic phases (bottom); (b) An overview EDX mapping separates the oxide phases into a Mn–rich and a Zn–rich oxide. (c) High magnification EDX mapping shows that the interface layer consists of Al_2O_3 and Cr_2O_3 .

Table 2

Quantified EDX spectra of the highlighted areas in Fig. 7c. For the quantification, a mean thickness of 200 nm and density of $5,5 \text{ g/cm}^3$ is used.

Area	Element	Element concentration in at.%				
	0	Al	Cr	Mn	Fe	Zn
А	27,2	0,1	0	0,3	14,2	58,0
В	72,4	0,1	0	4,0	0,2	23,1
С	73,6	0,0	0	20,8	0,2	5,2
D	66,7	15,2	2,1	3,5	1,9	10,4
Е	68,2	0	12,7	2,0	1,8	15,1

 Mn_2O_4 . According to the EDX-data, Mn based spinel carries trace amounts of Fe, which can replace Zn or Mn as well.

4. Discussion

Based on the microscopy and spectroscopy characterization during this work, a better understanding on the role of steel alloying elements in the formation of specific oxides was obtained. Chemical analysis with SEM and AES on a μ m scale left some oxide phases unidentified due to the limits of the spectroscopic techniques in the uppermost coating layer. Complementary, high magnification TEM investigations on nm–scale showed complex oxide formations along the interface between the oxide and the Fe–Zn intermetallic phases.

Table 3

Quantified EDX spectra in the highlighted areas in Fig. 8c. For the quantification, a mean thickness of 200 nm and density of 5.5 g/cm^3 is used.

Area	Element concentration in at.%						
	0	Al	Cr	Mn	Fe	Zn	Nb
А	29,2	0,5	0	0	50,3	19,8	0
В	84,0	0,9	0,2	4,5	1,0	1,1	8,1
С	71,3	11,6	5,7	0,6	1,8	7,4	1,5
D	70,0	28,0	0	0	0,2	1,7	0
Е	72,8	0,7	0	1,6	0,6	24,9	0

The main question was how the different alloy compositions influence the formation of the surface oxide layer during the annealing process. Focusing on the differences in the alloy and coating compositions, the investigated specimens can be divided into 2×2 groups. A first distinction was based on the coating type (GI or GA). A second distinction was made with respect to the alloy composition. HX340LAD and 20MnB8 are steel grades with no Cr as alloying element, while 22MnB5 and 22MnCrB8–2 contain low amounts of Cr.

The brittle ZnO layer is lifted off the intermetallic Fe–Zn phase creating large cavities with diameters of several μ m. Bellhouse and McDermid [30] found that different thermal expansion coefficients of oxides and Fe were responsible for chipped off oxides during annealing and quenching on TRIP steel. Chen et al. [15] confirmed this behavior



Fig. 8. TEM lamella of a HX340LAD + GI (200 s > 870 °C) sample; (a) STEM-HAADF image shows the multi–phase, polycrystalline oxide–layer (center) and Fe–Zn phase (bottom left); (b) Overview EDX mapping of the indicated area reveals two different oxide phases (Mn– or Zn–rich); (c) High magnification EDX mapping with focus on the initial Al₂O₃ layer.



Fig. 9. TEM–SAD analysis of a single Mn–rich oxide grain on a 20MnB8 + GA (200 s > 870 °C) sample; The TEM–BF image (a) shows the applied SAD aperture and indicated EDX measurements as given in Table 4; The acquired diffraction pattern (b) fits the simulated diffraction pattern (c) for ZnMn₂O₄.

in a dual phase steel similar to the investigated steel grades. Due to the storage of the specimen in standard atmosphere, the Zn patina was already altered and formed $Zn(OH)_2$ [31] as HIM–ToF–SIMS measurements confirmed.

Al is necessary as part of the galvanizing bath but not necessarily a desired element in the alloy composition. After hot–dipping, a faint Al₂O₃ layer is immediately formed on top of the Zn coating [7,17]. In all examined samples, a thin Al₂O₃ film was detected, separating the main oxide layer from the intermetallic Fe–Zn phases. This layer can either originate from the hot–dipping process or can form later during austenitization annealing in the press hardening furnace. In direct comparison of GI and GA coatings, the noticeably thicker Al₂O₃ in GI coated specimens is a result of a higher Al content in the galvanizing bath. The Al₂O₃ layer is often heavily fractured and remnant clusters of small particles are incorporated into the intermetallic Γ –phase (see Fig. 10b). The Al₂O₃ acts as a barrier, where precipitates of other alloying elements are trapped. In areas where the whole oxide is lifted off the Fe–Zn phases, Al₂O₃ is mostly found at the bottom side of the oxide and not on top of the intermetallic Fe–Zn phases (see Fig. 10a,c).

The main alloying elements of the investigated specimen is Mn, and thus the most common oxide–forming element beside Zn and Al. Mn is used to alter the austenitization condition of the steel. EDX measurements combined with SAD revealed that Mn does not occur as a simple native oxide, e.g. MnO, Mn_2O_3 or MnO_2 but in form of a mixed spinel (Mn,Zn)Mn_2O_4. Autengruber et al. [17] reported the spinel to be hausmannite Mn_3O_4 (MnO + Mn_2O_3), but the measurements in this work suggest a substitution of MnO by ZnO within the spinel crystal. Thus, a slightly different $ZnMn_2O_4$ spinel, a mineral called hetaerolite, is formed. The measurements showed a small amount of Fe in the spinel grains, hinting at an additional replacement of Mn by Fe [32]. However, the concentrations were low and occasionally not detectable. The spinel oxide was found in the main oxide layer above the Al_2O_3 separation, predominantly embedded in ZnO (see Fig. 10a–d).

A common addition in hot–forming steel alloys is Cr, which further changes the austenitization condition similarly to Mn. In the bare steel sheet, Cr forms an oxide acting as corrosion protection close to the surface. The most common native oxide is Cr_2O_3 in corundum form, which is the only oxide stable at the annealing temperature of 890 °C [33,34]. Previous measurements suggested a high affinity of Cr_2O_3 to the original Al_2O_3 layer. During annealing, Cr_2O_3 particles seemed to attach onto the steel side of the Al_2O_3 layer, forming an additional thin diffusion and oxidation barrier (see Fig. 10b,d). This behavior was observed for high Cr alloyed steels but to a lesser degree also in low Cr alloyed steels. In sufficient concentrations, the Cr_2O_3 layer acts as a replacement at the interface between oxide and the Fe–Zn intermetallic phases. At the interface the damaged Al_2O_3 layer was supplemented with Cr_2O_3 , repairing the barrier.

Si was added as an alloying element acting as a deoxidizer in the steel matrix in similarly low amounts as Cr. Nevertheless, SiO_2 is a common product on top of the Zn coated steel sheets. Due to the very high stability of SiO_2 , the heat treatment has no effect on the oxide and precipitates can move freely in liquefied Zn and Zn–Fe coatings. Eventually, these precipitates will appear on top of the intermetallic Fe–Zn phases and form small structures underneath the Al_2O_3 separation layer (see Fig. 10a).

Nb was found as sub μm sized oxide particles trapped at the Al_2O_3 layer. Presumably the most common compound is Nb₂O₅, which is thermodynamically stable below 1512 °C [35]. Due to the very low concentration of Nb in the steel alloys, precipitates were rarely detected.

HIM ToF–SIMS investigations on GA coated specimen revealed the coexistence of oxides and hydroxides as part of the uppermost layer as predicted by Lindström and Wallinder [36]. Moreover, a locally restricted appearance of OH phases (see Fig. 6c) is visible underneath the uppermost coating layer, suggesting that conversion of ZnO to Zn(OH)₂ takes place underneath the surface. Presumably, water droplets penetrate the upper oxide layer through cracks and accelerate the conversion process, since the evolution from oxide to hydroxide only happens if H_2O is available.

Based on the presented observations and assumptions, a schematic model to describe the oxide formation is proposed in Fig. 11. The model is explained by focusing on GI coated specimens, but is adaptable for

Table 4

Quantified EDX spectra in the highlighted areas in Fig. 9a.	. As the sample is very thin in the shown area, a i	mean thickness of 100 nm and density	of 5,5 g/cm ³ is used
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Area/mineral	Formula	Element concentration in at.%			Crystal parameters		
		0	Mn	Fe	Zn	a in Å	c in Å
А	-	63,95	25,19	0,79	10,07	-	-
В	-	57,83	1,18	0,30	40,69	-	-
Hetaerolite	ZnMn ₂ O ₄	57,14	28,57	-	14,29	5,74	9,15
Hausmannite	Mn ₃ O ₄	57,14	42,86	-	-	5,76	9,44
Zincite	ZnO	50,00	-	-	50,00	3,25	5,21



Fig. 10. Overlays of EDX maps on STEM-BF images for GI coated specimens 22MnB5 (a), HX340LAD (b) and GA coated specimens 22MnCrB8-2 (c), 20MnB8 (d).



Fig. 11. Schematic of four important oxide–forming stages during press hardening annealing showing only the dominant Fe–Zn phases and the main oxide–formation of Al, Zn and the main alloy elements.

GA coated samples, where the initial structure is similar to a fully δ -phase transitioned Stage II instead of Stage I.

Before heating up in the press hardening furnace (Stage I), the layered structure consists of the steel substrate, containing alloying elements like Si, Cr or Mn and the coating, consisting of Al and Zn. Due to the proximity to the steel–sheet surface, these elements are mainly oxides as a result from selective oxidation from the hot–dip galvanizing annealing process. The steel matrix is separated from the Zn coating by a thin Fe_2Al_5 inhibition layer, which acts as a diffusion barrier. Due to the low Al additions in the liquid Zn bath and the high affinity of Al to O, a several nanometers thick Al_2O_3 layer covers the coating.

Stage II depicts the diffusion of Fe and alloying elements into the Zn coating, either through galvannealing (in the hot–dip galvanizing process) or during heating up in the press hardening furnace to about 550 °C. This results in a transformation of Fe and Zn into intermetallic Fe–Zn phases. In most cases, liquid Zn is completely transformed into solid Fe–Zn phases deforming the outermost surface, which can lead to a first cracking of the Al_2O_3 layer. In particular, this holds for GA coated samples, where this stage is the starting point for the austenitization annealing. Due to the low Al content in the liquid Zn bath and the GA process, Al_2O_3 occurs only in fragments on the surface but not as a continuous layer. During the phase transformation, small alloy particles move through the whole coating, eventually reaching the Al_2O_3 layer.

After the specimen reaches a temperature of 665 °C, a transition from δ - to Γ -phase occurs (Stage III). A consequence of the phase transformation and the heating rate is a volume change of the coating, further deforming the Al₂O₃ layer. Due to the induced strain on the oxide layer, it breaks apart into smaller particles which can be incorporated in the Fe–Zn phase [18].

At the final annealing temperature of 890 °C (Stage IV), the Fe–Zn phase has already been decomposed at 780 °C into Zn saturated α-Fe and liquid Zn. The α -Fe grains start to grow from the steel substrate toward the surface and push the alloying elements and their oxides in the same direction. In GI coated steel strips, Al dissolved in the liquid Zn can repair the already existing Al₂O₃ layer. Moreover, in both coatings, the remaining Al can lead to a formation of a new Al₂O₃ layer in the early stages during the liquefaction of the coating. However, the Mn containing liquid Zn can protrude through the broken Al₂O₃ layer. There, Mn and Zn react with O to form the spinel (Mn,Zn)Mn₂O₄, depending on the availability of Mn. When Mn has been depleted in the fluid, another layer of ZnO is formed, covering most of the spinel. The high thermodynamic stability and low density of SiO₂ lead to an expulsion from the liquefied Zn coating. Therefore, SiO₂ can be found on top of the final Fe-Zn intermetallic phases not surpassing the Al₂O₃ layer. Cr2O3 is extremely stable with a melting point of 2435 °C and thus is unaffected by the annealing process. Cr2O3 shares the same corundum crystal structure with Al₂O₃, explaining the high attraction of Cr₂O₃ to the initial Al₂O₃ layer. If the layer is unharmed, Cr₂O₃ is accumulated on the steel side, increasing and strengthening the former pure Al₂O₃ layer. However, in case of fracturing during the previous stages and the availability of Cr in sufficient concentration, Cr2O3 can regenerate the interface by replacing the missing Al₂O₃. A similar behavior was found in Fe-20Cr-25Ni-Nb austenitic stainless steel by Chen et al. [37], although the initial oxide was Cr_2O_3 instead of Al_2O_3 .

5. Conclusion

In this work, the oxide composition of eight different Zn and Zn–Fe coated steel sheets with either 45 s or 200 s austenitization holding time were analyzed by AES and EDX in a SEM, ToF–SIMS in a HIM and EDX and SAD in a (S)TEM. All specimens were hot–dip galvanized and half of them were additionally galvannealed. The used techniques allowed to investigate the oxide distribution on a range from several μ m down to a few nm.

The presented results showed that the main part of the oxide layer consists of ZnO, which eventually transforms to $Zn(OH)_2$ over time in

ambient atmosphere. The dominant polycrystalline ZnO layer is accompanied by a spinel oxide (Mn,Zn)Mn₂O₄, where Mn and Zn substitute each other. Additionally, low amounts of Fe from the steel substrate were found along the spinel phases. A thin Al₂O₃ film, originating from low Al additions in the Zn bath, usually separates the primary oxide layer from Fe-Zn phases. Moreover, the oxide layer is often lifted off from the subjacent intermetallic Fe-Zn phases. Thus, the faint Al₂O₃ layer is attached to the bottom side of the oxide layer but not onto the intermetallic Fe-Zn phases. Additionally, phase transformations during austenitization annealing lead to volume changes, which can damage the otherwise closed Al₂O₃ coating. Remnants from these cracks are clusters of small Al₂O₃ particles and were found in the Γ -phase. If Cr is available from the steel alloy, it acts as an enhancement for Al, attaching to the Al₂O₃ layer and oxidizing to Cr₂O₃. Typically, Cr is not found on the surface, which suggests that it was already oxidized before annealing (e.g. by selective oxidation). During annealing, the (Al,Cr)₂O₃ layer behaves like a filter in the liquid Zn, which allows only Zn and Mn to pass through leading to the formation of oxides, but traps precipitates of other elements like Nb.

CRediT authorship contribution statement

Wolfgang Gaderbauer: Investigation, Visualization, Formal analysis, Data curation, Methodology, Writing - original draft. Martin Arndt: Investigation, Formal analysis, Writing - review & editing. Tia Truglas: Investigation, Formal analysis, Writing - review & editing. Nico Klingner: Investigation, Formal analysis, Writing - review & editing. Nico Klingner: Investigation, Formal analysis, Writing - review & editing. David Stifter: Resources, Writing - review & editing. Josef Faderl: Conceptualization, Validation, Project administration, Writing - review & editing. Heiko Groiss: Resources, Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs and the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged.

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