



Influence of stripping and cooling atmospheres on surface properties and corrosion of zinc galvanizing coatings

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ABSTRACT

In this work the influence of stripping/cooling atmospheres used after withdrawal of steel sheet from Zn or Zn-alloy melt on surface properties of Zn (Z) and Zn-Al-Mg (ZM) hot-dip galvanizing coatings has been studied. The aim was to understand how the atmosphere (composed by nitrogen (N₂) or air) affects adhesion strength to model adhesive and corrosive behaviour of the galvanized substrates. It was shown that the surface chemical composition and Volta potential of the galvanizing coatings prepared under the air or nitrogen atmosphere are strongly influenced by the atmosphere. The surface chemistry Z and ZM surfaces prepared under N₂ contained a higher content of metal atoms and a richer hydroxide density than the specimens prepared under air atmosphere as assessed by X-ray photoelectron spectroscopy (XPS). The induced differences on the microstructure of the galvanized coatings played a key role on the local corrosion induced defects as observed by means of in situ Atomic force microscopy (AFM). Peel force tests performed on the substrates coated by model adhesive films indicate a higher adhesive strength to the surfaces prepared under nitrogen atmosphere. The obtained results have been discussed in terms of the microstructure and surface chemical composition of the galvanizing coatings.

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1. Introduction

Hot-dip galvanized steel is widely used as a structural material for various applications including complex shapes and structures like in car bodies. In the latter various metallic parts are traditionally joined by point welding or fastening. Recently the adhesive bonding is growing as an alternative joining technology especially in the case of multi-material structures. It offers important benefits such as good mechanical properties, additional stiffening effect, and reduction of galvanic corrosion between the joined parts [1]. However, de-adhesion or delamination of the adhesive joint may occur when exposed to a corrosive environment. De-adhesion is a consequence of the degradation of the polymer-metal interface [2]. The damaged interface may easily stay unnoticed due to the complexity

and high cost of the techniques available for the inspection of adhesive joints. The consequences of the degradation of adhesive joints can be more structurally deleterious than the corrosion degradation of painted metals due to the loss of mechanical integrity of the joint.

Therefore it is important not only to ensure the high adhesion strength between the metal surface and an adhesive layer but also guarantee the durability of the joint under corrosive environment. The joint performance in terms of adhesion and durability relies heavily on the surface chemistry of metal substrates as well as the characteristics of the interface between an adhesive and the metal surface. Targeted pre-treatments on galvanizing coatings such as substrate cleaning or application of adhesion promoters may improve the adhesion strength to organic matrixes [3,4]. The surface properties of zinc galvanizing layers may also be modified during the galvanizing process [5].

In the hot-dip galvanization process a ferrous substrate is immersed in a bath of molten zinc or zinc alloy at around 450 °C. During immersion the metal piece is covered by a layer of zinc with Fe-Zn phases closer to the interface. The formation of the latter can

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be inhibited by adding typically 0.1–0.3 wt.% of Al to the galvanizing bath. Iron diffusion to zinc is inhibited by Fe_2Al_5 intermetallic layer which improves the performance of the galvanized coating [6,7]. In the last decades various zinc coatings containing Al and Mg additions or other coatings based on Al alloys have been developed as promising substitutes to common zinc galvanizing coatings. Such coatings present better properties compared to conventional zinc hot-dip galvanizing ones [8–10]. Among these one can mention the superior corrosion protection in environmental corrosion tests. Such behaviour is obtained due to the specific microstructure of the alloys obtained during the galvanizing process. The operating parameters of the galvanizing process such as the bath temperature, dipping time, line speed can be optimized to control the efficiency of the zinc coating formation during the immersion step [11]. After the dipping process the thickness of the galvanizing coating can be controlled by the stripping (air knife wiping) process. In this process wiping dies remove an excess of liquid zinc metal from the surface with a gas stream. After the galvanization is complete the substrates are subjected to either cooling or additional heat treatment.

The composition of the gaseous mixture during the stripping or cooling processes may affect the surface oxide film chemistry and the microstructure of the galvanizing layer. Consequently, the different chemistry of the surface oxide films and zinc coatings microstructure may affect the adhesion properties and corrosion performance. Adhesion strength at metal–adhesive interface is mainly governed by the adsorption theory taking into account the intermolecular contact between atoms. This interaction can be produced through van der Waals, acid-base and covalent interactions [12]. The latter largely contribute to the adhesion strength due to the high energy of the formed bonds. In the adhesion process both substrate and adhesive chemistries including the hydroxyl content [13], functional groups and surface oxide thickness [14] are important.

The composition of the galvanizing bath mainly determines the coating microstructure [15]. However, air knife wiping, cooling process, bath temperature and the time of immersion can also affect the coating microstructure [16,17]. This in turn influences the susceptibility to corrosion and the localized corrosion behaviour of the galvanized layer due to the existence of phases, which have higher activity than the zinc solid solution [18]. When a galvanized layer is covered by an adhesive (or organic coating) the localized corrosion process at adhesive–metal interface may largely contribute to de-adhesion process [19]. Therefore, the understanding of the local corrosion phenomena on zinc galvanizing coatings is required for prediction of a possible de-adhesion tendency in adhesive joints.

The knowledge of the factors affecting surface chemistry, microstructure and corrosion behaviour of zinc galvanizing coatings is important for improving the adhesion strength and inhibiting or delaying the de-adhesion during aging in a corrosive environment. The aim of this work was to study the surface and electrochemical properties of steel galvanized with Zn and Zn–Mg–Al alloys prepared in a hot-dip galvanizing simulator. In particular the effects of stripping/cooling atmospheres on the surface chemical composition, the localized corrosion susceptibility and the adhesion strength to a model adhesive were investigated by means of spectroscopic, microstructural, electrochemical and mechanical techniques.

2. Experimental

2.1. Materials

Zinc galvanized samples were prepared in a hot-dip galvanizing simulator at Salzgitter Mannesmann Forschung GmbH. A 0.8 mm

thick steel sheet of grade S320GD was used as substrate. Two galvanized coatings were produced: a common hot-dip layer with around 0.3 wt.% of aluminium (Z), and a coating containing around 1–2 wt.% of Al and Mg (ZM). The thickness of the produced coatings was around 25 μm . The thickness was adjusted by a high pressure gas stream (stripping process) which blows excessive zinc off the galvanized surface. After this process the coated steel sheets were cooled at the same cooling rate. Ambient air and nitrogen (N_2) atmospheres were used in the stripping and cooling processes. Two extreme conditions were used: stripping $-\text{N}_2$ and cooling $-\text{N}_2$ (samples Z(N_2) and ZM(N_2)) and stripping–air and cooling–air (samples Z(air) and ZM(air)).

The galvanized samples prior to the studies were cleaned sequentially in Acetone, 2-propanol and absolute ethanol solvents in ultrasonic bath during 10 min in each step, then dried and stored in a desiccator.

Ultrapure Millipore™ water >18 MOhm.cm was used for preparation of 5 mM NaCl (99.5 wt.% purchased from Aldrich) solution having pH around 6.

2.2. Techniques

2.2.1. XPS

X-ray photoelectron spectroscopy was used to study the influence of stripping and cooling atmosphere treatments and aging process on the surface chemistry of Z and ZM. X-ray photoelectron spectra were recorded with an Omicron ESCA + System (Omicron NanoTechnology GmbH, Germany), utilizing a Al $K\alpha$ X-ray source and a spot diameter of 600 μm , with a step size of 0.05 eV at a constant pass energy of 25 eV and a base pressure of $<2.10^{-9}$ mbar. The take-off angle was set to 60° with respect to the surface plane. The spectra were fitted with the CASA XPS software using a Shirley background and a mixture of Gaussian and Lorentzian fitting for the peak shapes. For the quantification, relative sensitivity factors supplied from Omicron GmbH were implemented in the CASA XPS database. All spectra were calibrated using the C1 s peak (binding energy (BE) = 285 eV) as internal reference.

2.2.2. SEM/EDS

Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) studies of surface microstructure and elemental composition were performed by FEG SEM system Hitachi SU-70 with accelerating voltage 25 kV.

2.2.3. AFM/SKPFM

Atomic Force Microscope (AFM) Digital Instruments NanoScope III system with Extender™ Electronic Module was used for the acquisition of topography and Volta potential maps on the polished adhesive–zinc–steel cross-section and polished zinc plane surface. Topography was acquired in tapping mode when the tip was in intermittent contact with the substrate. For the Scanning Kelvin probe force microscopy (SKPFM) measurements AFM was operated in the interleave mode with two pass scans. The first pass acquired the topography of the surface. During the second scan the tip was lifted up from the surface by 100 nm and the ac voltage of 5 V 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 to obtain the map of the Volta potential difference (VPD). Topography and VPD maps with surface area 20 by 20 μm were obtained. For all SKPFM measurements, silicon probes covered with Cr/Pt layers were used. Measurements were performed at around 23 ± 1 °C and $55 \pm 3\%$ RH. Volta potential values of metal substrates are presented versus standard hydrogen electrode (SHE). For that firstly VPD potential of a pure Ni surface was measured [20],

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