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Influence of magnesium content on the corrosion resistance of the cut-edges of Zn–Mg-coated steel

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ABSTRACT

The ability of Zn–Mg coatings (with magnesium content between 5.8 and 15.5 wt.%) to protect steel sheets has been evaluated with local electrochemical techniques (scanning vibrating electrode technique, microcapillary electrochemical cell) and rotating disk electrode, and compared with the corrosion protection afforded by a pure zinc coating. From immersion tests of coated steel cut-edges, it is observed that alloying zinc with magnesium leads to a decrease of the galvanic current between the coating and the steel surface, and to an improvement of the steel corrosion resistance after a drying period, due to the presence of magnesium in the corrosion products.

1. Introduction

Since several decades zinc coatings are widely used to protect steel sheets from atmospheric corrosion. It is well known that the durability of the protection depends directly on the zinc coating thickness. However, for economic reasons there is a strong need to develop thinner coatings, using more environmentally friendly processes such as physical vapour deposition (PVD) [1–4]. Consequently, research efforts have focused on the development of novel compositions for sacrificial coatings, which would be more efficient than a pure zinc coating to protect the steel. Alloying zinc with other elements such as magnesium and/or aluminium have been proposed in several studies [4–8] to improve corrosion resistance and self-healing properties of sacrificial coatings, both for automotive and roofing applications. This improvement of self-healing properties was observed on the cut-edge of the coated steel after different corrosion tests (cyclic corrosion tests, salt spray test, humid cabinet), and related to a decrease of the period before red rust precipitation and paint delamination. It was also observed that the decrease of the corrosion current is also significantly pronounced for Zn–Mg alloys in comparison with pure zinc coatings [5]. However, based on long-term (ten years) atmospheric corrosion tests, it was found that a significant magnesium content in the coating is required, at least 0.04%, to obtain an improvement of the corrosion resistance [9]. On the contrary, above 8% of magnesium content, the weight loss of Zn–Mg coatings would be higher than that of zinc coatings according to a study on model alloys [10]. Some authors propose that magnesium favours the formation of corrosion products that act as cathodic inhibitors (simonkolleite, MgO and $Mg(OH)_2$) while preventing the formation of the non-protective corrosion product ZnO [5,10–13]. It has also been shown that a magnesium rich film is formed beneath zinc corrosion products [10].

This work aims at comparing efficiency, in terms of corrosion behaviour on the cut-edge electrodes, classical hot-dip galvanized steel with PVD deposited Zn–Mg coatings. The corrosion behaviour of galvanized steel cut-edges immersed in a low concentrated NaCl solution has been already studied in previous papers using local electrochemical probes (Scanning Vibrating Electrode Technique, electrochemical microcapillary cell, local pH probe) and numerical models [14,15]. Two complementary protective mechanisms have been highlighted. The first one is the cathodic polarization of the bare steel surface by the sacrificial coating, leading to the formation of a zinc based hydroxide/oxide film on the steel surface next to the coating, controlled by the pH at the metal/solution interface. This film has the ability to inhibit the cathodic reactions (mainly oxygen reduction). This inhibition has a beneficial effect during the wet phase of the atmospheric corrosion resulting in a decrease of the overall electrochemical activity of the cut-edge. According to Krieg et al. the inhibition of oxygen reduction results from a chemical modification of the iron oxide by zinc cations, instead of a zinc based hydroxide/oxide film formation [16]. The second protection mechanism is provided by white corrosion products of zinc (mainly $Zn(OH)_2$) formed in the bulk of the electrolyte and covering the steel surface. These products could act as a barrier layer

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limiting the steel corrosion and the occurrence of red rust precipitation. This process occurs when the saturation of zinc hydroxide is exceeded, i.e. when a large amount of zinc coating is dissolved and/or if the electrolyte thickness is low, e.g. during the transition from a wet to a dry phase of an atmospheric or cyclic corrosion test. Such a transition also induces an increase of the electrolyte resistance leading to a loss of the cathodic protection of the steel surface by the zinc coating [17]. It highlights the challenge to optimize the right balance between both protective mechanisms to improve the corrosion protection of novel Zn–Mg sacrificial coatings. In the following work, the influence of magnesium on these protective mechanisms is shown and the benefit of this element for the corrosion resistance of coated steel sheet is discussed.

Table 1
Composition and thickness of Zn and Zn–Mg coatings.

Designation	Coating composition (weight%)	Steel thickness/ mm	Coating thickness/ µm	Thickness ratio steel/coating
Zn–5Mg	Zn balance Mg 5%	3	3	1000
Zn–6Mg	Zn balance Mg 5.8%	2.9	2.9	1000
Zn–15Mg	Zn balance Mg 15.5%	2.9	2.9	1000
Zn	Zn	5	40	125

2. Experimental

2.1. Samples

Zn–Mg coatings were deposited on steel plates using a PVD technique. Zn–Mg alloys of different compositions were heated in a crucible placed in a vacuum chamber (Pressure of about 10^{-7} mbar). X-ray diffraction analysis showed that the structure of the coatings was microcrystalline. Fig. 1 shows a typical micrograph of the coating after N_2 fracture. No defects such as pinholes could be detected on the coating. Moreover the PVD coating was extremely compact, except on its outer surface where a columnar structure could be observed over a thickness of c.a. 0.3 µm.

Table 1 details the composition and the thickness of Zn–Mg coatings deposited by PVD on one side of steel sheets. Mg content varies from 5 to 15.5 wt.%. The thicknesses of the steel sheet and of the Zn–Mg coating were always the same for a better comparison of results. Indeed the thickness ratio steel/coating will influence the magnitude of the galvanic coupling between the steel and the coating (the larger this ratio the higher the coupling current), and the steel area ratio, in the vicinity of the coating, affected by the deposition of Zn–Mg corrosion products. Additionally, a one-side hot-dipped galvanized steel sheet is included for comparison.

The steel sheets were cut into coupons of 30 × 15 mm that were embedded vertically in an epoxy resin (Huntsman™) cured at room temperature. The exposed cut-edge was ground with SiC paper up to the grade 4000 and then, with diamond solution up to the grade 1 µm. The polishing was finished by cleaning with ethanol in an ultrasonic bath for several minutes. An optical observation of the surface with a microscope was performed in order to ensure that the coating was not damaged during the polishing.

2.2. Current distribution measurements

A commercial scanning vibrating electrode technique (SVET) (from Applicable Electronics™) was used with the ASET software (Science Wares™). The setup has been detailed by Ogle et al. [18]. Our setup is equipped with two cameras, perpendicular and parallel to the sample surface. For all experiments, the electrolyte thickness was 3 ± 0.2 mm. This electrolyte thickness was controlled visually with the lateral camera. Local current densities over the cut-edge were recorded at fixed height of 150 µm, with steps of 25 µm. Scans were performed perpendicularly to the cut-edge length. For each measurement, the current density was averaged during 1 s after a waiting period of 0.5 s.

2.3. Local polarization curves

Local polarization curves were performed on the cut-edge by using microcapillary electrochemical cell (MEC) technique. Glass microcapillaries were prepared using a capillary puller (Suter Instruments™) and grounded to adjust the inner diameter of the tip around to 100 µm. A silicone seal (Dow Corning® 732) was deposited at this tip to avoid solution leakage. The microcapillary was inserted in a small container containing a Pt wire as counter electrode (CE), and filled with a 1 M NaCl solution. A short bridge allowed the contact with a saturated calomel electrode (SCE). The small container was mounted on the rotating carousel of an optical microscope. The set-up was placed in a Faraday cage. Potentiodynamic polarization curves were performed by sticking the microcapillary, filled with a 1 M NaCl solution, on the sample surface. The potential was controlled with a high resolution potentiostat (Jaissle Electronic™1002T-NC-3). Anodic or cathodic polarization curves were plotted starting from the open circuit potential (OCP), with a scan rate of $1\ \mathrm{mV\,s^{-1}}$. Before local polarization curves, cut-edge samples were immersed during 14 h in the same conditions as for SVET measurements. Then they were washed with distilled water and dried with a flux of dry air.

2.4. Rotating disk electrode (RDE)

RDE technique was used to quantify the cathodic inhibition of oxygen reduction on a steel electrode in solutions containing Zn^{2+} and Mg^{2+} at different concentrations. A 4 mm diameter sized iron disk electrode, mounted in epoxy resin, was ground until 4000

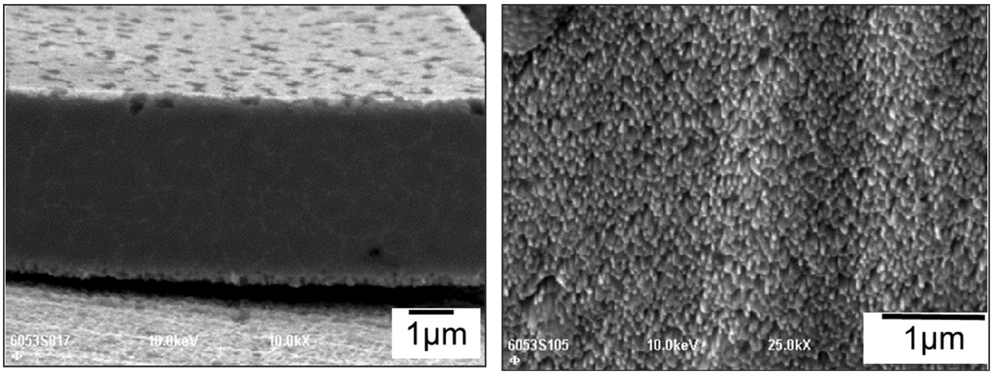

Fig. 1. SEM images on the section of a Zn–15Mg coating after N_2 fracture (Right: top view of the coating).