Effect of the microstructure of Zn-Al and Zn-Al-Mg model alloys on corrosion stability

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ABSTRACT

Zn-5Al and Zn-3Al-2Mg model alloys were cast and heat treated in order to obtain specimens with distinct microstructures and identical chemical compositions. The microstructure was characterised in detail to identify composition, size and distribution of present phases. Mass losses of samples with different microstructures and identical chemical compositions that were subjected to a cyclic corrosion test and a test under non-rinsing conditions differed by a factor of up to two. The mechanism is discussed based on measurements of corrosion stability of individual phases and chemical and phase compositions of corrosion products.

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1. Introduction

In order to improve long-term corrosion stability and reduce costs of zinc coated steel products, great efforts are invested into optimization of the zinc coating composition by alloying. Successful examples of the development are coatings alloyed with aluminium, Zn-5Al (Galfan) and Zn-55Al (Galvalume[TM], Zincalume[TM]). At present, the main development activity is focused on Zn-Al-Mg coatings. Whereas Zn-Al coated steel sheets are mostly coil coated and applied in the building industry, Zn-Al-Mg materials are being adopted also for home appliance and automotive applications [1–6].

A large body of scientific literature is available on the effect of the microstructure of aluminium and magnesium alloys on corrosion [7–9]. It is believed that the microstructure of zinc alloy coatings is strongly affecting their corrosion properties as well. Recent publications indicate that the microstructure induced by alloying especially with Mg might play a key role in the formation of protective layers [10,11]. It was suggested that a finer microstructure induced by the alloying prevents extreme local pH values by averaging the pH in anodic and cathodic sites, which in turn leads to the formation of layers of higher protective quality. Elvins et al. reported for Zn-5Al coatings that different microstructures at identical compositions can have an effect on the corrosion behaviour [12]. Although the volume fraction of primary zinc dendrites remained unchanged at higher cooling rate from the melt, the larger number of smaller non-interconnecting dendrites had a positive effect on the corrosion resistance. Elvins et al. also investigated the effect of very low Mg additions in the range of 0.05 wt.% [13]. The additions caused an increase in the zinc dendrites volume fraction from 6 to 22%. The authors found by scanning vibrating electrode technique (SVET) measurements during 24-h exposure in 5% NaCl solution that this microstructural modification boosted cut edge corrosion.

As demonstrated for Zn-5Al coatings, there is a space for improving the coating corrosion stability and overall product durability by tailoring the coating microstructure [12,13]. This is of utmost practical importance since the market volume for alloy coatings of different compositions is growing due to their superior corrosion and other functional properties [1–29]. The aim of this work was to study the role of the Zn-Al(-Mg) microstructure under atmospheric corrosion using model alloys. It is a part of a larger project devoted

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to the impact of microstructure of the coatings on their corrosion behaviour [30].

2. Experimental

2.1. Sample preparation and microstructure characterisation

Model alloys Zn-5Al (ZA1, ZA2, ZA3), Zn-3Al-2Mg (ZAM1, ZAM2, ZAM3), Zn-6Mg (ZM6) and Zn-16Mg (ZM16), as well as pure zinc (Zn) and aluminium (Al) were prepared by induction melting in a graphite crucible under protective atmosphere of 99.5% argon. Purity of raw Zn, Mg and Al was 99.99, 99.99 and 99.5 wt.%. After introduction to a crucible, metals were heated up to 750 °C and kept at the temperature for 6 h to dissolve and homogenize. For Zn, the temperature was 600 °C and the holding time 1 h. Then, still under the argon atmosphere, the melt was poured into a brass mould and solidified at cooling rate of about 3 K s^{-1}. Cylindrical casts were of 50 mm in diameter. They were cut to round samples of 50 mm in diameter and about 3 mm thick.

In order to obtain distinctly different microstructures, Zn-5Al and Zn-3Al-2Mg casts were heat treated under different regimes. Heat treatment temperatures and holding times were selected arbitrary. Chemical compositions measured by X-ray fluorescence (XRF), heat treatment parameters and hardness for the prepared materials are given in Table 1.

Alloy microstructures were studied after grinding and polishing by scanning electron microscopy (SEM) with back scattered electron (BSE) imaging under magnification from 100× to 25,000× using apertures 60–120 μm and accelerating voltage of 20 kV. Mean sizes and distances of phases were measured in SEM micrographs using Kappa Imagebase software for at least 50 particles in 5 different micrographs. The phase composition was analysed by X-ray diffraction spectrometry (XRD) and energy dispersive X-ray spectroscopy (EDX).

As reference, non-passivated line hot-dip coated steel panels of Zn-0.2Al (HDG), Zn-5Al (G) and Zn-2Al-2Mg (ZAM) with the coating thickness of 20 μm were used.

2.2. Corrosion testing

Flat round samples cut from the casts were subjected to accelerated corrosion tests and the mass loss was measured. The samples were grinded down to 400 grit and their backsides masked with tape. Reference panels of HDG, G and ZAM were cut to 50 × 50 mm and their backside and edges masked with tape. The exposed area of 1960 mm^2 was identical for both types of samples.

ECC1 is a cyclic accelerated corrosion test developed and used by the automotive industry [31]. It is conducted at 35 °C and comprises humid (90% relative humidity, RH) and dry (55% RH) phases. Aqueous salt solution containing 1 wt.% NaCl at pH 4 is sprayed over the samples during 30 min once a day. Four parallel samples were exposed to 42 daily cycles with total duration of 6 weeks. Corrosion products were removed in saturated glycine, NH$_2$CH$_2$COOH, water solution at 20 °C following the ISO 8407 standard [32] and the mass loss measured. Chromic acid (100 g L^{-1} CrO$_3$, 10 g L^{-1} AgNO$_3$) was used to remove corrosion products from aluminium. Run-off water collected under the exposed samples and solutions obtained by the corrosion product dissolution were analysed for Zn, Al and Mg using inductively coupled plasma mass spectrometry (ICP-MS).

Samples pre-contaminated with 1.4 g m^{-2} chloride as NaCl dissolved in methanol were exposed to a 4-week non-rinsing corrosion test (static test) at 80% RH and at 20 °C. Solution of 7.54 g L^{-1} NaCl in methanol (>99.5%) was applied to the sample surfaces. On each sample of 1960 mm^2, 600 μl of the solution was applied in 6 separate doses of 100 μl each using a micropipette. In all cases,

the solution on the sample surface was uniformly spread with a micropipette tip and dried out before the application of the next dose. This procedure ensured even distribution of salt deposits over the surface. Further details on the procedure are given elsewhere [14]. Mass loss was measured after removal of corrosion products as described above.

2.3. Electrochemical measurements

Open circuit potential E_{corr} and anodic and cathodic polarisation curves for model alloys freshly abraded down to emery paper 600 in ethanol were measured by direct current (dc) electrochemistry in aqueous NaCl solutions at different pH and at 20 °C under stirring. E_{corr} was recorded for 10 min and then either cathodic or anodic polarisation curve measured from +20 mV or −20 mV vs. E_{corr} to −1.2 V or −0.85 V vs. saturated calomel electrode (SCE), respectively, with the scan rate of 0.2 mV s^{-1}. 4.6 M NaCl solution forming in equilibrium between NaCl and humid air at 80% RH and at 20 °C [33] was prepared and the pH adjusted with HCl and NaOH to 4, 7 and 10. In addition, experiments were carried out in a diluted 10 mM NaCl solution at pH 7. The solutions were in contact to air before the measurements to get saturated with oxygen. SCE and platinum wire were used as the reference and counter electrode, respectively. The working electrode was made of a piece of model alloy embedded in epoxy resin with an exposed area of 500 mm^2.

2.4. In situ IRRAS measurements of corrosion product formation

Initial formation of corrosion products was followed in situ by infrared reflection absorption spectroscopy (IRRAS). The experimental cell consisted of a stainless steel body with KRS-5 (thallium bromo iodide) windows. The cell is built to fit a Harrick's multi-reflection accessory providing an angle of 78° vs. the surface normal of the incident light. The in situ IRRAS measurements were performed with a Varian FTS 7000 spectrometer, equipped with a KBr beam splitter and a DTGS detector, by adding 500 scans at a resolution of 8 cm^{-1}. IRRAS spectra were recorded as single beam spectra before and after introduction of humid air at 85% RH and then after different times during the exposure in humid conditions. Spectra were obtained by taking the ratio of a single beam at a certain exposure time vs. a single beam spectra obtained after 5 min exposure to humid air or in dry air. The in situ studies were performed on polished samples of 19 × 22 mm. A small amount of a saturated solution of NaCl in ethanol was deposited on the surface with a pipette leading to a surface concentration of approximately 70 mg m^{-2} Cl$^-$.

3. Results and discussion

3.1. Microstructure of model alloys

3.1.1. Identified phases

Four principal phases were identified in the studied alloys: η phase with hexagonal close-packed (hcp) structure containing beside zinc up to 1.5 wt.% Al; α and β solid solutions with face-centred cubic (cF) structure composed of zinc and aluminium; and Mg$_2$Zn$_{11}$ phase with primitive cubic (cP) structure and space group $Pm3$ [34] with 6–7 wt.% Mg and up to 1 wt.% of dissolved Al. The β phase has a theoretical Al content of 22 wt.% but our measurements showed 17–30 wt.% Al. The α phase typically contained between 40–70 wt.% Al. Compositions of the identified phases determined by EDX at high magnification are given in Table 2.

3.1.2. Zn-5Al, ZA1–ZA3

Fig. 1 shows the Zn-Al phase diagram (A) and the Zn-rich corner of the same (B). The nomenclature and also the appearance of