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Corrosion mechanism of model zinc–magnesium alloys in atmospheric conditions

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ABSTRACT

Recently, superior corrosion properties of zinc coatings alloyed with magnesium have been reported. Corrosion behaviour of model zinc–magnesium alloys was studied to understand better the protective mechanism of magnesium in zinc. Alloys containing from 1 to 32 wt.% magnesium, pure zinc, and pure magnesium were contaminated with sodium chloride and exposed to humid air for 28 days. Composition of corrosion products was analyzed using infrared spectroscopy (FTIR), ion chromatography (IC), and Auger electron spectroscopy (AES). The exposure tests were completed with scanning Kelvin probe (SKP) and electrochemical measurements. Weight loss of ZnMg alloys with 1–16 wt.% magnesium was lower than that of pure zinc. Up to 10-fold drop in weight loss was found for materials with 4–8 wt.% Mg in the structure. The improved corrosion stability of ZnMg alloys was connected to the presence of an Mg-based film adjacent to the metal surface. It ensured stable passivity in chloride environment and limited the efficiency of oxygen reduction.

1. Introduction

The application of steel construction materials is largely connected to the use of protective metallic coatings containing zinc. These coatings provide barrier and galvanic protection to steel substrate applied in automotive, building, and other industries, improving durability and aesthetic properties of final products. To extend the lifetime of steel constructions and save costs, big efforts have been exerted to optimize zinc coating composition by alloying it with e.g. aluminium, iron, and nickel.

First trials to improve corrosion stability of zinc coatings with magnesium date back to the 1960s [1]. Commercial products such as Zn–11Al–3Mg–0.2Si and Zn–6Al–3Mg for heavy corrosive environments have been available from the end of 1990s. Presently, several European steelmakers are developing Zn–Mg(–Al) coated products for building and automotive applications using either more traditional hot-dipping in baths containing magnesium [1] or a physical vapour deposition (PVD) technology [2–4]. In the latter case, magnesium is applied in a thin layer on the surface of electro galvanized (EG) or hot dip galvanized (HDG) zinc sheets by PVD in vacuum. The zinc–magnesium alloy is consequently formed by diffusion of magnesium into the zinc coating under elevated temperature exceeding 250 °C [2].

Although the available data seem to indicate only a very limited effect of magnesium in coatings with up to 1 wt.% Mg in both atmospheric and aqueous environments [5–7], it was clearly demonstrated by several research groups that alloying of zinc coatings to a higher content of magnesium significantly improves their corrosion resistance in atmospheric conditions [1–4,8–10]. Vlot et al. [1] informed about corrosion properties of a newly developed zinc coating containing 1.5–2.0 wt.% of magnesium and the same quantity of aluminium produced by hot-dipping. The coating consists of Zn grains surrounded by a eutectic of Zn and $MgZn_2$. The time to red rust formation relative to a reference HDG coating with identical thickness in a salt spray test was up to 20 times longer. Koll et al. [2] reported a considerable improvement of corrosion performance of Zn–Mg coated steel produced as a combined approach of hot-dipping and PVD-coating. Apart of η-Zn phase, the ZnMg coatings contained mainly the intermetallic phase $MgZn_2$ and some Mg_2Zn_{11}. Formation of red rust in humidity, salt spray, and cyclic corrosion tests was delayed with a factor of 8–13 compared to the HDG reference. Similarly encouraging results were shown by Schwerdt et al. [3] for Zn–Mg coatings with the total thickness of 7.5 μm produced in a combined EG/PVD process. A layer of $MgZn_2$ intermetallic phase with a thickness of 0.8–1.6 μm on a base zinc coating improved the corrosion resistance by a factor of 10 in comparison to conventional EG sheets at the same coating thickness. An extraordinary improvement in corrosion performance in the salt spray test was shown also in Refs. [4,8]. Hosking et al. [9,10] tested similar coatings consisting of about 2-μm $MgZn_2$ layer on an EG-deposited Zn layer of 6 μm in a standard automotive laboratory corrosion test comprising cycles of humidity, drying and intermittent spraying with 1 wt.% NaCl solution at pH 4.2. The time to

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appearance of significant red rust was 3 times longer for ZnMg compared to the EG and HDG references.

Although the results are very promising, it must be noted that they were obtained under specific conditions of few selected accelerated tests. To make zinc–magnesium coatings acceptable for industrial applications, much broader corrosion studies must be conducted to define their application limits. Moreover, with the exception of Hausbrand's electrochemical studies of $MgZn_2$ phase [11,12] and the recent paper by Hosking et al. [9], there are very limited open literature resources on the mechanism of magnesium protection in zinc coatings. The aim of this study was to understand better the role of magnesium in the corrosion mechanism of zinc–magnesium exposed to air in the presence of chloride. As composition of ZnMg coatings is often non-equilibrium and it is complicated to prepare well-defined coatings with a wide range of magnesium concentrations, model alloys were used in this study.

2. Experimental

2.1. Preparation and composition of model alloys

Preparatory conditions of model ZnMg alloys were adjusted according to the phase diagram in Fig. 1 [13]. Zinc was melted and $ZnCl_2$ flux was added at the temperature of 450 °C. Magnesium was set in at the temperature by 50 K higher than the temperature of liquidus of each alloy. The melt was strongly homogenized by a graphite bar and poured into a mould with a quatrefoil section. Rods of 20 mm in diameter were prepared from the casts by mechanical machining and cut to 6 mm high samples.

Chemical composition of the alloys given in Table 1 was determined using energy dispersive X-ray analysis (EDX). The content of impurities was lower than 0.01 wt.%. Phase composition was measured by X-ray diffraction (XRD). The microstructure was studied after etching by an agent containing CrO_3, Na_2SO_4 and water. It is shown in Fig. 2 for selected alloys.

Composition of alloys ZnMg6 and ZnMg16 was selected to be as close as possible to that of pure phases Mg_2Zn_{11} and $MgZn_2$, respectively. In order to obtain equilibrium phase structures, ZnMg6 and ZnMg16 castings were homogenized by annealing at temperatures of 360 and 320 °C, respectively, for 15 h.

Phase composition of ZnMg1 and ZnMg2 alloys was similar, consisting of Zn dendrites and Zn + Mg_2Zn_{11} eutectic in the interdendritic area. ZnMg4 and ZnMg8 contained $MgZn_2$ polyhedrons with irregular borders due to the peritectic reaction $L + MgZn_2 = Mg_2Zn_{11}$. The space between the polyhedrons was filled with Zn+Mg_2Zn_{11} eutectic. The annealed ZnMg6 alloy composed of Mg_2Zn_{11} matrix with remnants of $MgZn_2$ phase. The structure of ZnMg16 consisted purely of $MgZn_2$ phase. ZnMg32 alloy formed

Table 1
Chemical and phase composition of model ZnMg alloys

Alloy	Zn [wt.%]	Mg [wt.%]	Phase composition[a]
Zn	99.99	0.00	η-Zn
ZnMg1	98.92	1.07	67% η-Zn, 33% Zn + Mg_2Zn_{11} eutectics
ZnMg2	97.90	2.09	65% Zn + Mg_2Zn_{11} eutectics, 35% η-Zn
ZnMg4	95.77	4.22	71% Zn + Mg_2Zn_{11} eutectics, 29% $MgZn_2$
ZnMg6	93.77	6.22	83% Mg_2Zn_{11}, 17% $MgZn_2$
ZnMg8	92.06	7.93	53% Zn + Mg_2Zn_{11} eutectics, 47% $MgZn_2$
ZnMg16	84.89	15.10	$MgZn_2$
ZnMg32	68.64	31.35	51% Mg + MgZn eutectoid, 49% MgZn
Mg	0.00	99.99	Mg

[a] Approximate volume fraction of each phase was obtained by image analysis.

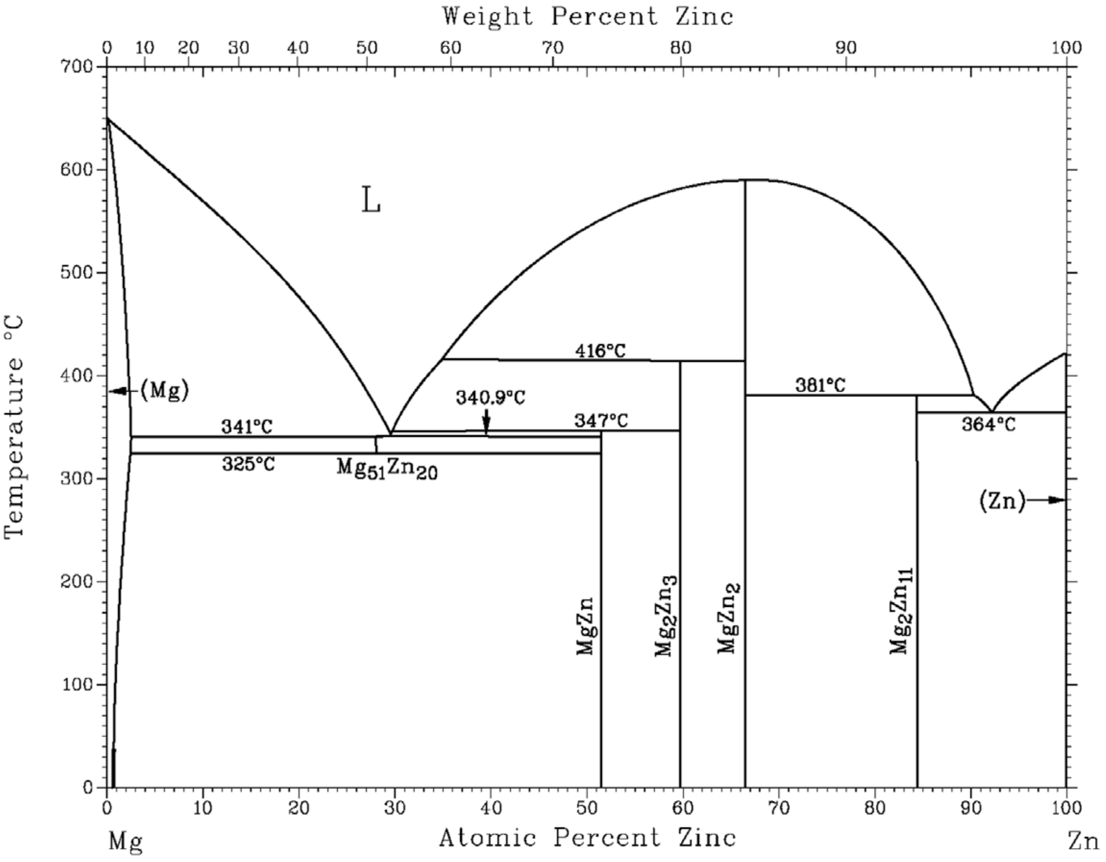

Fig. 1. Mg–Zn phase diagram [13].