Available online at www.sciencedirect.com
SCIENCE DIRECT®
Electrochimica Acta 51 (2005) 77–84
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Influence of the alloying component on the protective ability of some zinc galvanic coatings

N. Boshkov [a,*], K. Petrov [b], D. Kovacheva [b], S. Vitkova [a], S. Nemska [b]

[a] *Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev", Bl. No. 11, Sofia 1113, Bulgaria*
[b] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev", Bl. No. 11, Sofia 1113, Bulgaria*

Received 2 January 2005; received in revised form 2 March 2005; accepted 19 March 2005
Available online 17 May 2005

Abstract

The composition of the corrosion products of pure Zn galvanic coatings as well as of some zinc alloys (Zn–Mn and Zn–Co) after treatment in selected free aerated model media (5% NaCl and 1N Na_2SO_4) is studied and discussed. X-ray diffraction and X-ray photoelectron spectroscopy investigations are used for this purpose. It is concluded that the corrosion products (zinc hydroxide chloride hydrate in 5% NaCl and zinc hydroxide sulfates hydrates in 1N Na_2SO_4) play a very important role for the improved protective ability of the zinc alloys toward the iron substrate, compared to the pure Zn coatings. Another result is that, for a given medium, the corrosion products are one and the same for both alloys independently of the fact that the alloying component is electrically more positive or negative than the zinc. Some suggestions about the models of the appearance of these products and their protective influence are also discussed.

Keywords: Corrosion; X-ray diffraction; Photoelectron spectroscopy; Zinc; Zinc alloys

1. Introduction

Zinc galvanic coating on steel substrates provides good mechanical properties, weldability, paintability as well as good corrosion resistance [1–4]. Generally, in the case of corrosion attack, zinc protects the iron or steel substrate by sacrificial protection—its layers are covered with oxidized products known as "white rust". The corrosion resistance of zinc could be improved by using additional treatment—chromating or phosphating films, another type surface finishing or by alloying with some 3D-metals like Co, Ni, Mn, Cr and Fe [2–5]. All these alloys exhibit higher corrosion resistance (protective ability toward the substrate) compared to the individual metals [6–10].

Most of the zinc galvanic alloys used in practice contain metals that show electrically more positive potential than the zinc itself, for example, Co, Ni, Sn, Fe and Cr. The Co is more preferred from an economical viewpoint. Considerably high protective ability in corrosion media containing Cl^- ions or SO_2 has been reported for Co contents as low as 1–5 wt% [5,11–13]. This alloy is a solid solution of cobalt in the zinc (η-phase) with a hexagonal close packed structure.

Contrary to all above-mentioned metals, manganese has electrically more negative potential compared to the zinc and is the only metal that can be co-deposited with Zn from water solutions. High protective ability of this alloy is usually achieved at manganese amounts in the range from 40 up to 60 wt% [8,14], although lower concentrations have been also successfully used [9,10,15–17].

This article describes and specifies the protective action of the alloying component in two representative types of zinc galvanic alloys (namely, Zn–Mn and Zn–Co) during the corrosion treatment compared to the pure zinc coatings.

* Corresponding author. Tel.: +359 2 979 3920; fax: +359 2 971 26 88.
E-mail address: nbojkov@ipchp.ipc.bas.bg (N. Boshkov).

0013-4686/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.03.049

2. Experimental

2.1. Galvanic coatings (thickness ~12 μm, hexagonal close packed structure)

2.1.1. Zn–Mn alloy coatings

Galvanic Zn–Mn alloys were electrodeposited from a starting electrolyte (SE) (in g/l): $ZnSO_4 \cdot 7H_2O$ 10.0; $MnSO_4 \cdot H_2O$ 100.0 and $(NH_4)_2SO_4$ 60.0. The process was carried out in a double-chamber cell (500 ml volume), current density 2 A/dm^2, pH value 5, 22 °C and continuous circulation of 150 rpm. Metallurgical zinc was taken for the anodes [18]. The phase composition of these alloys is discussed and described elsewhere [18,19]. Following alloy coatings were electrodeposited and investigated:

(a) Zn–Mn (~6 wt%), obtained by SE and two additives [18] with trade names AZ-1 (wetting agent 40 ml/1) and AZ-2 (brightener 10 ml/l). The additive AZ-1 contains poly-ethylene glycol and benzoic acid and AZ-2—benzalaceton and ethyl alcohol. This alloy forms a poly-phase coating—it consists generally in a pure zinc matrix with dispersed small zones of manganese and intermetallic compound $MnZn_7$ (known also as δ_1-phase from the phase diagram of metallurgical Zn–Mn alloys) [15,18].
(b) Zn–Mn (~11 wt%), obtained by SE and AZ-1 (20 ml/1)—the alloy contains mainly the intermetallic δ_1-phase and small of pure zinc inclusion zones [15,18].

2.1.2. Zinc–cobalt alloy coatings

Galvanic Zn–Co (1–5 wt%) alloys are obtained by using a starting electrolyte with a composition (in g/l): $ZnSO_4 \cdot 7H_2O$ 100.0; $CoSO_4 \cdot 7H_2O$ 120.0; NH_4Cl 30.0 and H_3BO_3 25.0. The electrodepositing conditions were: current densities 2–5 A/dm^2, pH value 3.0–4.0, room temperature 22 °C and metallurgical zinc anodes. Two laboratory additives (similar to AZ-1 and AZ-2), named ZC-1 (wetting agent 20 ml/l) and ZC-2 (brightener 2 ml/l) were also used [13].

2.1.3. Zinc coatings from a slightly acidic electrolyte

Zinc galvanic coatings were obtained from a sulfate bath containing (in g/l): $ZnSO_4 \cdot 7H_2O$ 175.0; $(NH_4)_2SO_4$ 25.0 and H_3BO_3 30.0 and deposition conditions: current density 2 A/dm^2; pH value 4.5–5.0; room temperature 22 °C and metallurgical zinc anodes. The additives used were AZ-1 (50 ml/l) and AZ-2 (10 ml/l) [13,15].

2.2. Sample sizes and corrosion media

Both sides of steel plates with sizes 20 mm × 10 mm × 1 mm were galvanically coated with pure Zn or with the alloys Zn–Mn and Zn–Co, respectively.

The protective ability of the coatings has been studied in two different corrosion media:

- model medium of free aerated 5% NaCl solution with pH ~ 6.7 at 22 °C—causes mainly local corrosion;
- model medium of free aerated 1N Na_2SO_4 solution with pH ~ 6.0 at 22 °C—causes local and general corrosion.

2.3. Sample characterization

2.3.1. X-ray diffraction (XRD)

The phase composition of the corrosion products was determined using X-ray diffractometer DRON-3 (Bragg–Brentano arrangement, Cu Kα radiation and scintillation counter).

2.3.2. X-ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out on an ESCALAB MkII (VG Scientific) electron spectrometer at base pressure in the analysis chamber of 1×10^{-8} Pa using Mg Kα X-ray source. Pass energy of the analyzer was 20 eV and the instrumental resolution measured as the full-width at a half-maximum (FWHM) of the Ag3d$_{5/2}$ photoelectron peak is 1.2 eV. Energy scale is corrected to the C1s peak maxima at 285 eV. Sample surfaces were studied after etching with accelerated argon (Ar) ions (for depth profiling) with energy of 3 keV and ionic current of 20 mA/cm^2.

2.3.3. Microprobe analysis

The elemental composition of the samples was determined using micro-probe analyzer JEOL Superprobe 733, Japan.

3. Results and discussion

3.1. Model medium of 5% NaCl

3.1.1. Zn–Mn alloys

3.1.1.1. X-ray diffraction. The diffraction patterns of both alloy coatings treated for 6 days in this model corrosion medium – Fig. 1B and C (Fig. 1A shows the spectra of non-treated δ_1-phase) – contain lines of Zn, NaCl and zinc hydroxide chloride hydrate $Zn_5(OH)_8Cl_2 \cdot H_2O$ (ZHC). The latter has very low product of solubility ($10^{-14.2}$) [20–22] that could be the most probable reason for the increased protective ability of this alloy, compared to the pure Zn [9,10,14,15]. It is obvious, that the coatings of the δ_1-phase Zn–Mn (~11 wt%), Fig. 1B – transform more easy to ZHC than the samples Zn–Mn (~6 wt%) – Fig. 1C. Probably, the homogeneous distribution of Mn in the intermetallic coating causes the nucleation and growth of uniform ZHC layer over the whole surface.

3.1.1.2. X-ray photoelectron spectroscopy. XPS spectra of zinc and oxygen for Zn–Mn (11%) alloy before and after corrosion treatment are presented in Fig. 2. It can be seen from the Zn spectra that the peak of this metal for corrosionally non-treated sample (No. 1) occurs at binding energy E_{bind} = 1022.5 eV. The literature data used [23,24], cor-