Surface & Coatings Technology 228 (2013) 221–228

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

The influence of anion type in electrolyte on the properties of electrodeposited Zn – Mn alloy coatings

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ARTICLE INFO

Article history:
Received 13 December 2012
Accepted in revised form 15 April 2013
Available online 23 April 2013

Keywords:
Electrochemical deposition
Zn – Mn alloy
X-ray diffraction (XRD)
Atomic force microscopy (AFM)
Corrosion

ABSTRACT

Zn – Mn alloy electrodeposition on steel electrode, in electrolytes containing chloride or sulfate anions, was investigated by chronopotentiometry. Galvanostatically obtained electrodeposits were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), and atomic absorption spectrophotometry (AAS). It was found that Zn^{2+} and Mn^{2+} ion reduction occurred at higher overpotentials in sulfate bath, leading to a higher Mn content in the deposit and smaller crystallites as compared to the chloride electrolyte. AFM images of deposits revealed that with the increase in deposition current density, bigger agglomerates formed in both electrolytes, leading to higher roughness and heterogeneity of the samples. In relation to this observation, the Zn – Mn coatings were deposited at current densities of up to 80 mA cm^{-2} because at higher current densities the samples from sulfate electrolyte were non adherent and dendritic. Depending on the deposition current density, the XRD patterns of the Zn – Mn deposits produced from chloride electrolyte indicated that the coatings were formed of either η- or ε-Zn – Mn phase, while the coatings obtained from sulfate bath consisted of ε-Zn – Mn phase. The linear polarization method showed that Zn – Mn alloys deposited from sulfate electrolyte exhibited higher corrosion resistance in NaCl corrosive media.

1. Introduction

Zn – Mn alloys offer several industrial applications. First of all, they have been developed with the aim of improving the corrosion resistance of Zn coatings on steel [1]. Although Zn has high corrosion resistance in most non-aggressive atmospheric environments, corrosion problems of zinc coatings are found in aggressive atmospheric environments where salt and sulfur dioxide are present. To overcome this problem, new types of zinc coatings, such as Zn – Ni, Zn – Co and Zn – Fe are currently being used in industry [2,3]. The Zn – Mn alloy was reported by several authors [4,5] to have even better corrosion resistance, particularly in aggressive media.

Zn – Mn alloys consist of paramagnetic Mn and diamagnetic Zn and it was reported that a change in Zn to Mn ratio in the alloy induced interesting changes in magnetic properties of the alloy. Therefore, there are potential magnetic applications of these alloys [6]. Finally, a large scale production of Zn – Mn alloys via electrodeposition is a promising method for recycling of spent Zn – Mn batteries, which represent up to 90% of the European battery market [7]. Hydrometallurgical process of recycling, namely, means that metals from batteries are dissolved in some solvent, for example HCl or H_2SO_4 [8]. If the next step in this process involves Zn and Mn recovery by electrodeposition, then the final product will be Zn – Mn coating [9].

Although Zn – Mn coatings may be obtained by hot-dip galvanizing [10], the most common production method is electrodeposition. Ionic liquids have been employed in electrodepositing of Zn – Mn alloys [11], but aqueous electrolytes are still much more used [5]. The standard electrode potentials of Zn^{2+}/Zn and Mn^{2+}/Mn couples in aqueous acidic medium are significantly different, -0.76 V/SHE for Zn vs. -1.18 V/SHE for Mn [12]. For this reason, various deposition parameters must be regulated in order to achieve co-deposition of less noble metal, Mn, with Zn. For example, it is known that the increase in Mn^{2+} ion concentration, shifting the deposition cathodic potential towards negative values, or the increase in deposition current density (c.d.), is beneficial for the increase in Mn % in the alloy [1,13], while stirring or heating of the electrolyte leads to the opposite effect [14,15]. Complexing agents play important role in the Zn – Mn deposition, because the complexation brings the Zn and Mn deposition potentials closer. Various complexing agents have been used until now, but often with some drawbacks. For instance, electrolytes containing citrate [6] or pyrophosphate [5,16] complexing agents are with low stability, because Mn(III) complexes precipitate in the solution. In addition, high stability constants of metal complex ions induce higher overpotential for metal reduction, leading to the low current efficiency [13,17].

However, two new types of electrolytes for Zn – Mn alloy deposition, namely, simple chloride electrolyte with H_3BO_3 [14] and simple

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Abbreviations: c.d., current density; Rp, linear polarization resistance; XRD, X-ray diffraction; AFM, atomic force microscopy; AAS, atomic absorption spectrophotometry.

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http://dx.doi.org/10.1016/j.surfcoat.2013.04.032

sulfate electrolyte with $(NH_4)_2SO_4$ [1] have appeared in literature in the last decade. Bearing in mind that these electrolyte types are very stable, both during storage and electrodeposition process, they could be good candidates for a commercial production of Zn – Mn coatings. So, the scope of the present work was to investigate the influence of the electrolyte type (chloride vs. sulfate) on the characteristics of the Zn – Mn alloys electrodeposited under the economically favorable conditions (room temperature, low deposition c.d., and without additives). The Zn – Mn alloys were obtained at constant c.d.s, and potential-time curves were recorded during the deposition. The composition, morphology, and structural properties of the Zn – Mn deposits were analyzed by atomic absorption spectrophotometry (AAS), Atomic Force Microscopy (AFM), and X-ray diffraction (XRD).

2. Experimental

Steel was used as substrate for electrodeposition, as a panel of 20 mm × 20 mm × 0.25 mm surface area. The steel substrates were pre-treated by mechanical cleaning (abrading successively with emery papers of the following grades: 280, 360, 800 and 1000) and then degreased in a saturated solution of NaOH in ethanol, pickled with 2 mol dm^{-3} HCl for 30 s and finally rinsed with distilled water. A Zn plate, placed parallel to the cathode, was used as a counter electrode in electrodeposition.

Electrodeposition was performed in electrolytes with two different compositions. Chloride electrolyte (pH 5.0) consisted of 1.8 mol dm^{-3} KCl, 0.4 mol dm^{-3} H_3BO_3, 0.4 mol dm^{-3} $ZnCl_2$ and 1.8 mol dm^{-3} $MnCl_2$, while sulfate electrolyte (pH 5.5) contained 0.6 mol dm^{-3} K_2SO_4, 0.5 mol dm^{-3} $(NH_4)_2SO_{4,}$ 0.4 mol dm^{-3} $ZnSO_4$ and 1.8 mol dm^{-3} $MnSO_4$. The metal ion concentration was the same in both electrolytes. Electrodeposition was carried out at room temperature (22 °C), in a single-compartment cell. All the employed electrolytes were prepared using p.a. chemicals and double distilled water. The Zn – Mn alloy was electrodeposited using PAR M173 potentiostat/galvanostat in galvanostatic mode, with c.d.s in the range of 20–80 mA cm^{-2}. The number of coulombs passed was tuned in order to ensure a coating thickness of ~10 μm, owing to the known current efficiencies.

Saturated calomel electrode (SCE) was a reference electrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of a substrate, was used to minimize errors due to *iR* drop in the electrolytes.

Corrosion measurements were performed in aerated 0.5 mol dm^{-3} NaCl solution. The linear polarization method was employed and the linear polarization resistance (R_p) was measured. Each working electrode was potentiodynamically polarized in the potential range between − 15 and + 15 mV (from cathodic to anodic) over the respective open circuit potential (OCP). Tafel plots were obtained at a scan rate of 0.2 mV s^{-1}, starting from the open circuit potential (OCP), after the constant OCP was established. Polarization tests were conducted using Gamry Reference 600 Potentiostat and three measurements were performed for each sample, with very good reproducibility.

NanoScope 3D (Veeco, USA) microscope was used to study the coating morphology by atomic force microscopy (AFM), which operated in tapping mode under ambient conditions. Etched silicon probes with spring constant 20–80 Nm^{-1} were used. AFM images were recorded over scan area of 1000 × 1000 nm^2. The agglomerate size dimension of electrodeposited coatings was determined from AFM image profile line analysis. The measurement was based on the assumption that the surface irregularities indicated by the profile line, represented the agglomerate size. In order to calculate the agglomerate size distribution, a hundred agglomerates were measured on each AFM image.

Structural analysis of the Zn – Mn alloys was studied by X-ray diffraction (XRD) on an Ital Structure APD2000 X-ray diffractometer in a Bragg–Brentano geometry using CuKα radiation ($\lambda = 0.15418$ nm) and step-scan mode (range: 30 − 90° 2θ, step-time: 0.50 s, step-width: 0.02). The program PowderCell [18] was used for an approximate phase analysis. Unit cell parameters were obtained by the least-squares method using the program LSUCRIPC [19]. The mean crystallite size was estimated from three most intensive diffractions peaks of the Zn – Mn (002), (100) and (101) planes, by the Scherrer formula [20] using the appropriate instrumental resolution function for ZnO as a standard.

For chemical composition analysis of Zn – Mn alloys, the alloys were stripped in a known volume of HCl, and metal ion concentration was determined by atomic absorption in AAS-PYE Unicam SP9, Philips.

3. Results and discussion

3.1. Electrodeposition of Zn – Mn alloy coatings

In order to study the anion effects on the electrochemical behavior and properties of Zn – Mn alloy coatings, the samples were electrodeposited galvanostatically, at c.d.s between 20 and 80 mA cm^{-2}, from sulfate and chloride electrolytes. A current efficiency for Zn – Mn electrodeposition was calculated by measuring the mass gain of the deposits, and a few data are presented in Table 1. As seen, the current efficiency in both electrolytes decreases with the increase in deposition c.d. In addition, the current efficiency is higher in chloride electrolyte, suggesting that h.e.r. is more inhibited in this solution. This is in accordance with literature data, since it is known that the overpotential for h.e.r. is significantly higher in the supporting electrolyte consisting of a chloride salt (KCl, NaCl), as compared to the corresponding sulfate salt, due to the stronger specific adsorption of Cl^- ions on the cathode surface [21].

Potentiometric *E*–*t* curves were recorded during the electrodeposition and some of the *E*–*t* curves are shown in Fig. 1. It can be seen that, depending on c.d. applied, the reduction overpotential was up to 70–180 mV higher in sulfate than in chloride electrolyte. To explain this, it has to be considered that Zn and Mn are present in form of various complex ions, as Table 2 depicts. When the formation constants are compared, it is clear from the table that higher formation constants are related to sulfate electrolyte, i.e. complex species of Zn and Mn in sulfate electrolyte are more stable as compared to the corresponding species in chloride electrolyte. Additionally, high constant values indicate strong Zn complexation with NH_3 in sulfate solution. So, this could be one of the reasons for higher overpotential and lower current efficiency in the sulfate electrolyte.

The observed higher current efficiency for metal deposition from chloride electrolyte could also be due to the fact that Cl^- anions catalyze Zn and Mn reduction process. Namely, there are plenty of articles describing the higher catalytic role of Cl^- ions, in comparison to SO_4^{2-}, in metal or alloy deposition associated with the h.e.r. Some examples are the deposition of Ni – Fe [27], Co – Fe [28], and Cu [29]. According to these data, Cl^- ions adsorbed on the cathode depress the h.e.r., and, in addition, metal-chloride complex species behave as an ion bridge between the cathode surface and the metal ion

Table 1
Deposition parameters and properties of Zn – Mn electrodeposits obtained from chloride and sulfate electrolyte.

Electrolyte type	Deposition c.d./mA cm^{-2}	Current efficiency/%	Crystallite size/nm	Unit cell parameters/nm		Polarization resistance/Ω cm^2
				a	c	
Chloride	30	100	–	–	–	653 ± 5
	50	90	66	0.2662	0.4953	603 ± 4
	70	85	37	0.2654	0.4950	590 ± 5
	80	80	18	0.2767	0.4476	535 ± 4
Sulfate	30	95	–	–	–	1601 ± 11
	50	85	19	0.2760	0.4459	1240 ± 8
	70	75	14	0.2764	0.4475	932 ± 8
	80	70	13	–	–	544 ± 4