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# Zinc electrodeposition from alkaline solution containing trisodium nitrilotriacetic added

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## ABSTRACT

An alkaline solution for the electrodeposition of Zn was developed, with trisodium nitrilotriacetic (NTA) as the complexing agent for Zn(II). The voltammetric studies showed that the NTA has a beneficial effect, displacing the initial reduction potential of Zn(II) species to more positive values than in its absence. Cyclic voltammetry of 1010 steel in alkaline Zn electrodeposition solution with 0.20 M NTA indicated the occurrence of the Zn underpotential electrodeposition, UPD, (regions wave $c'$ and $c''$) and followed by Zn overpotential electrodeposition, OPD (region peak $c'''$). The Zn electrodeposit produced voltammetrically at limiting potential ($E_f$) −0.81 V (region wave $c'$) was characterized by XRF and showed Zn presence. Zn electrodeposits produced potentiostatically at a potential −1.26 V were characterized by means of SEM, EDS and XRD. SEM results showed that fine-grain and compact Zn electrodeposits were obtained in the presence of 0.20 M NTA, at an electrodeposition charge density ($q_d$) of 10.0 C cm$^{-2}$. AFM analysis showed that the roughness of the Zn electrodeposits is greater in the presence than absence of 0.20 M NTA to both $q_d$ 2.0 and 10.0 C cm$^{-2}$. The adhesion test showed that the Zn electrodeposits, in general, had no area detached. The XRD pattern revealed that the Zn electrodeposits had a crystal structure with preferential orientation [0 0 2]. It was showed that NTA was a suitable complexing agent for the electrodeposition of Zn without dendrites and cracks.

## 1. Introduction

In previous work in this laboratory we investigated the electrochemical features of Zn electrodeposition and the chemical, physical and morphological characteristics of Zn electrodeposits on 1010 steel from alkaline sulfate solutions, in the presence and absence of various concentrations of disodium ethylenediaminetetraacetate (EDTA). It was shown, for example, that this chelating agent worked as a refiner of Zn electrodeposits [1].

In the literature, another complexing agent, NTA, an aminopolycarboxylate ligand, has been reported for Cu [2], Pb–Sn and Pb–Sn–Zn [3] Cu–Zn [4], Cd–S [5,6] electrodeposition, in the electrolytic recovery of metals [7] and in chemical electrodeposition of ZnS [8]. These papers showed that the NTA is a promising additive for these solutions.

Although the additives NTA and EDTA are similar, they may affect the Zn electrodeposition process differently, since different charged species can be formed at a specific pH, leading to Zn electrodeposits with, for example, distinct morphologies.

In light of this, in this study, NTA was added to an alkaline Zn solution and its effect on the electrodeposition process and on the electrodeposits were assessed. Cyclic voltammetry was utilized to study the electrodeposition process. The Zn electrodeposits prepared potentiostatically at −1.26 V were analyzed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and atomic force microscopy (AFM) to determine their morphology, chemical composition, structure and roughness, respectively. The average grain size of Zn electrodeposits was analyzed from SEM images. Zn electrodeposits obtained voltammetrically were analyzed by X-ray fluorescence (XRF).

## 2. Experimental

The working electrode (WE) was a disk (0.407 cm$^2$) of AISI 1010 steel, from CSN Co. (Brazil), which contained 0.04% P, 0.08% C, 0.3% Mn and 0.05% S. Before each experiment, it was polished with 600-emery paper, rinsed with distilled deionized water (ddw) and dried. The counter-electrode was a Pt plate (1.0 cm$^2$) and the reference electrode, to which all the potentials were referred, was a $Hg/Hg_2Cl_2/0.10$ M KCl electrode with an appropriate Lugging capillary. It must be stressed that all the potentials were recalculated and given in scale of standard hydrogen electrode (SHE). All electrochemical measurements were conducted at temperature of 25 °C.

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The electrodeposition solutions were: 0.10 M $ZnSO_4$ + 2.0 M NaOH, without and with 0.20 M NTA. All the reagents were of analytical grade and the water was ddw. The current efficiency (CE) was calculated from the stripping/electrodeposition charge ratio. In these tests, the Zn electrodeposits were electrodeposited potentiostatically with $q_d$ of 2.0 C cm$^{-2}$ and 10.0 C cm$^{-2}$. The stripping solution for the Zn electrodeposits was 1.0 M $NH_4NO_3$. The thickness ($\delta$) was determined by the following equation:

$$Q_{diss} = \frac{n\,\delta\,d\,A\,96,500}{MM} \quad (1)$$

where $Q_{diss}$, stripping charge (C); $n$, number of electron; $\delta$, thickness (cm); $d$, density of metal (g cm$^{-3}$); $A$, area of electrode (cm$^2$) and $MM$, molar mass (g mol$^{-1}$). Potentiodynamic curves were recorded with a GAMRY PCI-4 750 mA potentiostat/galvanostat. The surface morphology of electrodeposits was examined with a Phillips (XL 30 Oxford FEG) scanning electron microscope (SEM). EDS analysis of electrodeposits surfaces was done with a Zeiss/Leica SEM (LEO 440) and EDS Si/Li attachment, with ultrathin Be window. XRD patterns were produced with Cu K$\alpha$ radiation (1.5406 Å), using a Rigaku Rotaflex RU200B X-ray generator equipped with a goniometer, in $2\theta$ scanning mode (fixed $w = 2°$). The topography and roughness of the Zn electrodeposits was observed by AFM. The AFM images were produced with a Bruker Nanoscope V in the peak force tapping. The Zn electrodeposits analyzed by SEM, EDS, AFM and XRD were obtained at constant electrodeposition potential (−1.26 V) with $q_d$ of 2.0 C cm$^{-2}$ and 10.0 C cm$^{-2}$. XRF analysis was performed on Zn electrodeposits produced voltammetrically at $E_f$ −0.81 V, the electrodeposition continuing until the current density returned to zero, using a Shimadzu EDX 720. To determine the average grain size of the Zn electrodeposits, from the images obtained by SEM, was used the software ImageJ 1.47t, Wayne Rasband, National Institutes of Health – USA. For assessed the adhesion of the electrodeposits on the 1010 steel substrate was used Brazilian ABNT NBR 11003 standard [9] suitable for paints and varnishes adhesion tests [10,11]. For this test was used Scotch 880 3M adhesive tape. The adhesive tape was applied over the total area of the electrodeposit and removed by pulling it firmly at an angle close to 180° [9]. The adherence according to the ABNT NRB 11003 following the scale: $Gr_0$: no area detached; $Gr_1$: ≈5% area detached; $Gr_2$: ≈15% area detached; $Gr_3$: ≈35% area detached and $Gr_4$: ≈65% area detached.

The freshly obtained electrodeposits were vigorously rinsed with ddw, dried and put in an evacuated desiccator.

## 3. Results and discussion

### 3.1. Electrodeposition of zinc on 1010 steel substrate

$Zn^{2+}$ ions can form hydroxylated species, soluble or insoluble, depending on the pH of the solution. To avoid precipitation of Zn hydroxides, NTA can be added to complex the $Zn^{2+}$ ions. NTA also participates in acid/base equilibria and, to study the chemistry of Zn in solution with NTA, these equilibria must be considered, since the fraction of NTA ($\alpha$) available to complex $Zn^{2+}$ ions depends on the pH, similarly to EDTA [12]. It must be stressed that the $NTA^{3-}$ anion, fully deprotonated, exists (in significant amounts) only above pH 7.0.

In this study, the distribution of species as a function of pH (Fig. 1), involving the equilibrium constants for the formation of complexes of $Zn^{2+}$ ions with $OH^-$ and $NTA^{3-}$ and also for the NTA species, was derived from data in the literature [13,14]. The concentration of $[Zn(H_2O)_6]^{2+}$ complex (Table 1) was calculated for all the equilibria, involving the total $ZnSO_4$ concentration and the equilibria of $Zn^{2+}$ ions with $OH^-$ and $NTA^{3-}$ anions, by means of Eq. (2):

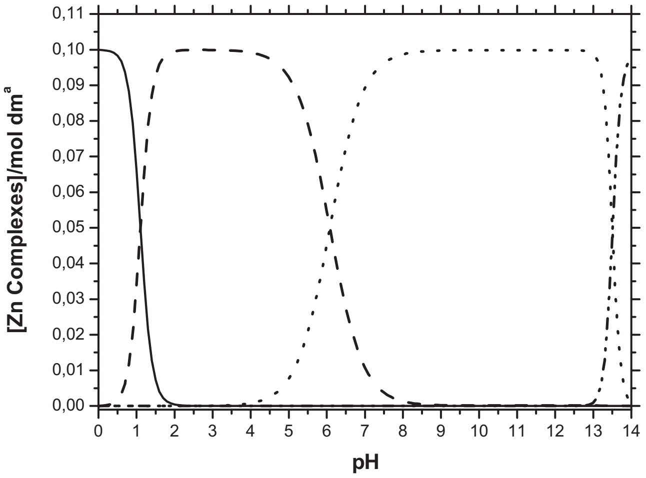

**Fig. 1.** Species distribution diagram as a function of pH, involving the equilibrium constants for the formation of complexes of $Zn^{2+}$ with $OH^-$ and $NTA^{3-}$. (——) $[Zn(H_2O)_6]^{2+}$, (- - -) $[ZnNTA]^-$, (······) $[Zn(NTA)_2]^{4-}$ and (-·-·-) $[Zn(OH)_4]^{2-}$.

**Table 1**
Concentrations of Zn(II) species present in electrolytic solutions of 0.10 M $ZnSO_4$ + 2.0 M NaOH, without and with 0.20 M NTA.

| NTA/M | $[Zn(H_2O)_6]^{2+}$/M | $[ZnNTA]^-$/M | $[Zn(NTA)_2]^{4-}$/M | $[Zn(OH)_4]^{2-}$/M |
|---|---|---|---|---|
| 0.0 | $1.45 \times 10^{-14}$ | 0.0 | 0.0 | $9.61 \times 10^{-2}$ |
| 0.20 | $7.23 \times 10^{-15}$ | $6.61 \times 10^{-5}$ | $5.02 \times 10^{-2}$ | $4.77 \times 10^{-2}$ |

$$[Zn(H_2O)_6]^{2+} = [ZnSO_4]/\{1 + (\beta_1 * OH^-) + [\beta_2 * (OH^-)^2] + [\beta_3 * (OH^-)^3] + [\beta_4 * (OH^-)^4] + [(\beta_{[ZnNTA]^-}) * \alpha * NTA] + [(\beta_{[Zn(NTA)_2]^{4-}}) * (\alpha * NTA)^2] \quad (2)$$

The $[Zn(OH)_4]^{2-}$, $[ZnNTA]^-$ and $[Zn(NTA)_2]^{4-}$ concentrations (Table 1) were calculated from $[Zn(H_2O)_6]^{2+}$ concentration by the following Eqs. (3)–(5):

$$\beta_{[Zn(OH)_4]^{2-}} = [Zn(OH)_4]^{2-}/[Zn(H_2O)_6]^{2+} * [(OH^-)^4] \quad (3)$$

$$\beta_{[ZnNTA]^-} = [ZnNTA]^-/[Zn(H_2O)_6]^{2+} * [\alpha * NTA] \quad (4)$$

$$\beta_{[Zn(NTA)_2]^{4-}} = [Zn(NTA)_2]^{4-}/[Zn(H_2O)_6]^{2+} * [(\alpha * NTA)^2] \quad (5)$$

where $\beta$ is the stability constant of the complex [13].

Fig. 2 shows voltammograms recorded from the 1010 steel substrate in electrolytic solutions containing 0.10 M $ZnSO_4$ + 0.20 M NaOH, without or with 0.20 M NTA.

In the electrodeposition arm of these voltammograms, in the absence of NTA, two cathodic peaks, $c_0$ (from ∼−0.90 V to ∼−1.18 V) and $c_1$ (from ∼−1.18 V to ∼−1.36 V), can be seen, while in the presence of 0.20 M NTA, three cathodic processes can be seen, viz., wave $c'$ (from ∼−0.61 V to ∼−0.87 V), wave $c''$ (from ∼−0.88 V to ∼−1.16 V) and peak $c'''$ (from ∼−1.17 V to ∼−1.36 V).

According to the data in Table 1 and Fig. 1 (species distribution diagram) without NTA, the predominant Zn(II) species in the solution was $[Zn(OH)_4]^{2-}$ (96.1%), whereas with 0.20 M NTA they were $[ZnNTA]^-$ (0.07%), $[Zn(NTA)_2]^{4-}$ (50.2%), and $[Zn(OH)_4]^{2-}$ (47.7%). The stability constant [10] of the $[ZnNTA]^-$ complex, $10^{10.66}$, is lower than those of $[Zn(NTA)_2]^{4-}$ and $[Zn(OH)_4]^{2-}$, respectively $10^{14.24}$ and $10^{14.82}$.