

# Corrosion resistance of ZnRE alloys

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## Introduction

In the field of cathodic protection of steel structures exposed to atmospheric and marine media, zinc is extensively used. Actually, compared to other metals with low redox potentials (like aluminium and magnesium), zinc is electrochemically active in a wide range of media but keep a relatively low dissolution rate. Anyway, service life of sacrificial anodes made of zinc could be improved (especially in very aggressive conditions) by the addition of alloying elements, which would decrease the dissolution rate of zinc but maintain its electrochemical potential low enough to avoid polarity reversal and keep the cathodic protective properties. Indeed, the natural corrosion layer on zinc, also named white rust is generally composed of voluminous, lamellar and not well-adherent products as zinc hydroxycarbonate  $Zn_4(CO_3)(OH)_6$  or  $Zn_5(CO_3)_2(OH)_6$ , or zinc hydroxisulfate [1-2]. To decrease the dissolution rate of zinc, a better adherence of the natural corrosion products layer is necessary. Rare earth metals are known to improve the high temperature made oxides on different metals [3-5]. Recently, some authors studied the effect on corrosion performance in aqueous media of rare earth metals contained in Zn-5%Al alloy (Galfan) [6-7]. They found that a small addition of rare-earth elements improves significantly the corrosion resistance of Zn-5%Al Galfan alloy through the formation of a “lanthanide-doped” corrosion product layer.

In this work, the corrosion resistance of ZnCe, ZnLa and ZnMischmetal alloys (Mischmetal = Ce/La : 75/25) is investigated. Particular attention is paid on the role of the intermetallic phases formed within the zinc matrix.

## Experimental

New Zn-RE<sub>1-2</sub> wt.% alloys (RE=Ce, La and Mischmetal: Ce 75%/ La 25%) were synthesized by melting under controlled atmosphere and cast in plates. Scanning electron microscopy, electron microprobe and X-ray diffraction analysis were performed to determine the microstructure of alloys. Their corrosion behavior was investigated in a reference corrosive medium, noted “ASTM water” (containing Na<sub>2</sub>SO<sub>4</sub> 148 mg L<sup>-1</sup>, NaHCO<sub>3</sub> 138 mg L<sup>-1</sup>, NaCl 165 mg L<sup>-1</sup> and simulating corrosion under atmospheric conditions) by using stationary electrochemical methods, electrochemical impedance spectroscopy, surface and cross section analysis after long-time immersion.

In parallel, the pure intermetallic phases Zn<sub>11</sub>Ce and Zn<sub>13</sub>La (formed within, the zinc matrix) were synthesized and their electrochemical influence was studied by voltametry and galvanic coupling.

## Results and Discussion

Microstructural analysis revealed that rare earth metal are exclusively present in intermetallic phases homogeneously dispersed in the zinc matrix (Fig.1): Zn<sub>11</sub>Ce in ZnCe alloys, Zn<sub>13</sub>La in ZnLa alloys and two substituted binary intermetallic phases in ZnMisch alloys, respectively Zn<sub>11</sub>Ce<sub>1-x</sub>La<sub>x</sub> and Zn<sub>13</sub>Ce<sub>y</sub>La<sub>1-y</sub>.

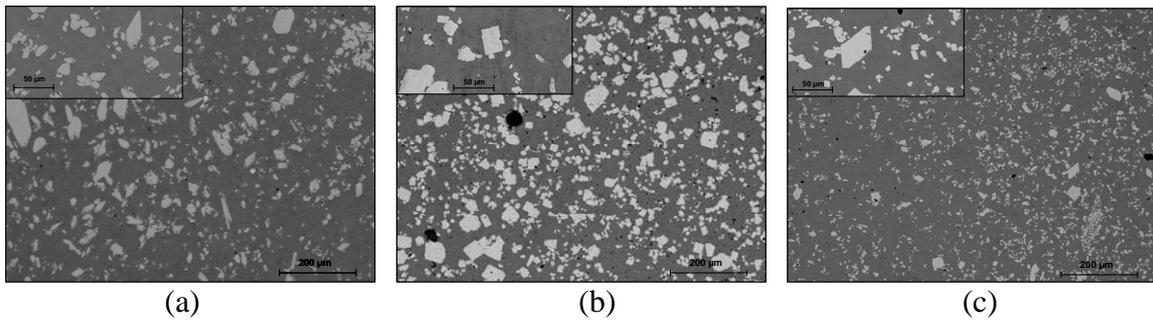


Figure 1: SEM images (BSE mode) of zinc alloys corresponding to (a) ZnCe 2 wt.%; (b) ZnLa 2 wt.%; (c) ZnMisch 2 wt.%.

The electrochemical properties of the ZnRE alloys are obviously linked with their composition and microstructure (Fig.2)

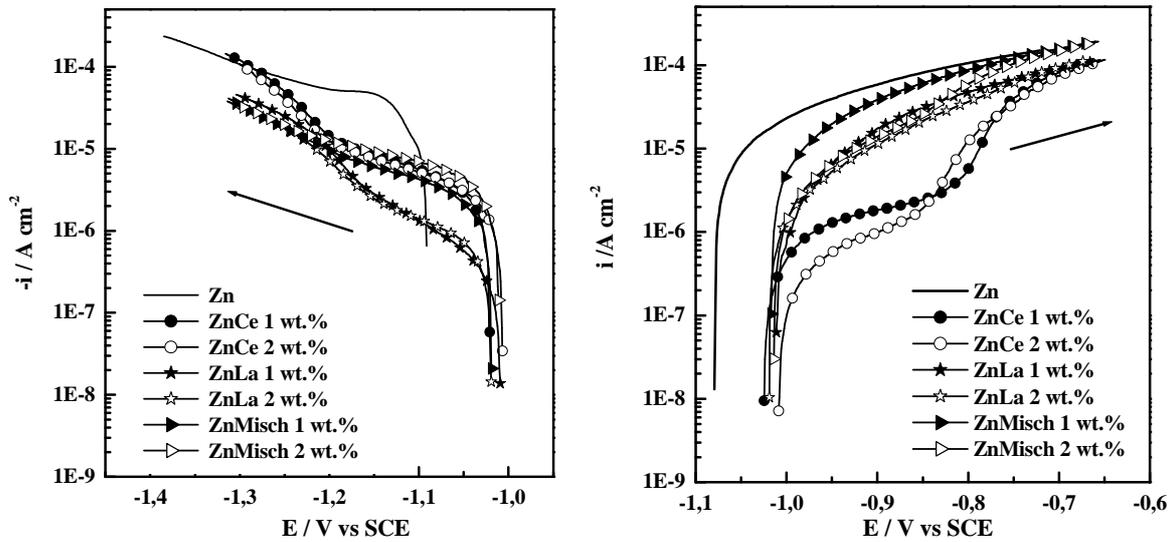


Figure 2: Cathodic and anodic potentiodynamic curves performed on ZnRE alloys after 24h immersion in ASTM water.

Actually, both intermetallic phases  $Zn_{11}Ce$  and  $Zn_{13}La$  act as preferential cathodic sites of dioxygen reduction and induce a cathodic inhibition of the corrosion of the Zn-RE alloys by comparison with pure zinc. This phenomenon is much more significant in the case of lanthanum containing alloys (Fig.3).

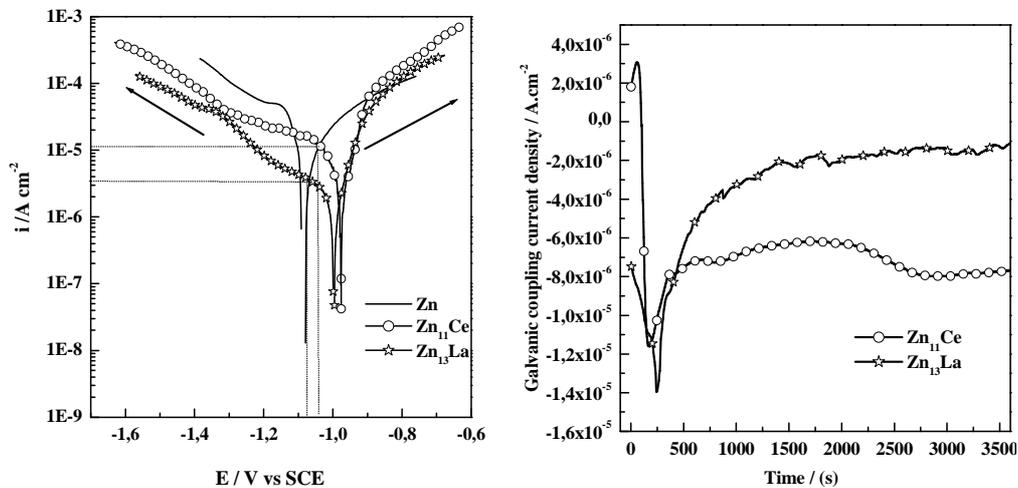


Figure 3: Corrosion properties of  $Zn_{11}Ce$  and  $Zn_{13}La$  intermetallic phases compared to pure Zn in ASTM reference water : Potentiodynamic curves performed after 24h immersion (left) ; Galvanic coupling (right).

In the specific case of cerium addition to zinc, an anodic inhibition was also observed and correlated with a chemical modification of the corrosion products (mainly made of hydrozincite) [8]. Actually, low quantities of cerium (less than 1 at.%) have been detected homogeneously in the corrosion layer by wave-length dispersive spectrometry (Fig.4a and b). From results of controlled precipitation experiments of cerium and zinc salts performed in carbonated medium, the presence of cerium in the corrosion layer and its protective character could be attributed to the formation of a mixed double lamellar zinc-cerium product (Fig.4c).

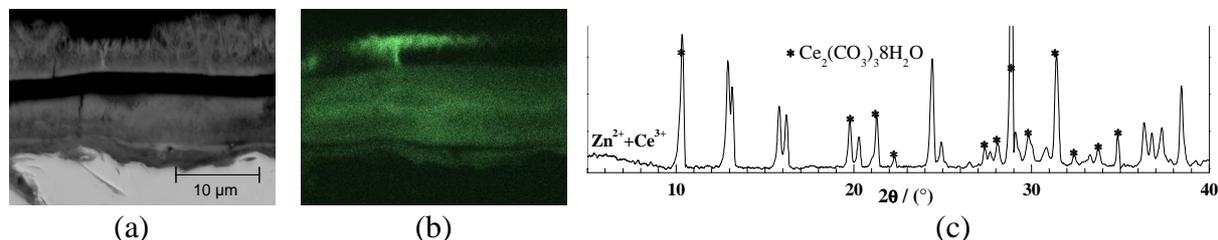


Figure 4: Cross-section corrosion layer of Zn-Ce<sub>2</sub> wt.% immersed 30 days in ASTM water: BSE image (a) and corresponding WDS X-Map of Ce (b); DRX pattern of a mixed double lamellar product (c) .

In the specific case of ZnLa alloys, the anodic inhibition described for ZnCe alloys, is not observed. Indeed, according to the results of the electrochemical study of the pure intermetallic phases, the intrinsic corrosion rate of Zn<sub>13</sub>La is lower than this of Zn<sub>11</sub>Ce, due to a more significant cathodic inhibition. Therefore it would be impossible to release La<sup>3+</sup> ions able to reinforce the protective properties of the corrosion layer (Fig. 5a).

In the case of ZnMisch alloys, no improvement of the corrosion resistance was observed due to the high corrosion rate of binary substituted intermetallic phases (Fig. 5b).

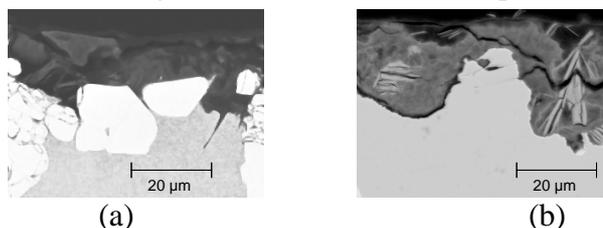


Figure 5: Cross-section corrosion layers of samples immersed 30 days in ASTM water: Zn-La<sub>2</sub> wt.% (a), Zn-Misch<sub>2</sub> wt.% (b)

In conclusion, addition to zinc of low quantities of cerium (less than 2 wt.%) or lanthanum (less than 1 wt.%) can improve the corrosion resistance of zinc. However, by increasing the rare earth content in the alloys, the galvanic coupling phenomenon becomes more important and makes the alloys less resistant than pure zinc.

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