



Microstructure and spatial distribution of corrosion products anodically grown on zinc in chloride solutions



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ARTICLE INFO

Keywords:

Simonkolleite
Zinc oxide
Microstructure
Corrosion

ABSTRACT

Zinc substrates were electrochemically oxidized in NaCl solution to produce corrosion patinas. XRD, XPS and Raman analyses enabled the identification of simonkolleite and zinc oxide as the patina constituents. FIB-SEM imaging shows that the upper part of the patinas is a network of simonkolleite nanosheets with an open microstructure that is unlikely to act as a significant barrier for corrosion processes. STEM investigations and Raman mapping measurements reveal the presence of a ca. 20–400 nm thin nanoporous ZnO-rich film below the simonkolleite and covering the zinc substrate. Under potentiostatic conditions, the reduced cathodic activity of the patina-covered zinc electrodes is assigned to this nanoporous ZnO layer.

1. Introduction

The ability of zinc (and its alloys) to achieve self-protection with patinas formed by corrosion products (CP) has been an important topic of research [1–3,6]. Yet there is still a significant lack of knowledge regarding the microstructure of corrosion products (CP) and the influence thereof on corrosion resistance of zinc. The latter is often expressed in terms of “barrier effect” that may hinder the transport of electroactive species around the electrode/electrolyte interface [3,4,7]. The concept of physical barrier is therefore directly related to the CP microstructure. However, in the field of zinc corrosion, few in-depth investigations have been dedicated to that matter [8–9]. This stands in contrast to other fields of electrochemistry in which microstructure plays a paramount role and cross-sectional electron microscopy analyses are regularly performed [10–13].

Simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) is one of the main corrosion products of zinc in chloride-containing environment [4,14–17]. However, its protective nature has not been unambiguously elucidated notably because limited microstructural data is available in the literature. Recently, Joo et al. investigated the corrosion of galvanized steel covered by synthetic simonkolleite obtained by dissolution of the zinc coating [4,5]. The pertinent rationale of their work was to study a single CP in order to better understand its protective properties. Yet ZnO was also detected along with simonkolleite and the microstructural analysis was limited to top-view and tilted SEM micrographs with relatively low

magnification. Therefore the microstructure effect of each CP could not be clearly assessed.

In this communication, zinc is anodically polarized in NaCl electrolyte. Stress is laid on cross-sectional electron microscopy analysis for gaining valuable insight on the microstructure, spatial distribution and barrier effect of the CP (simonkolleite and ZnO).

2. Experimental

2.1. Electrochemical cell

All electrochemical experiments were carried out at room temperature using a three-electrode configuration in a Teflon cell at the bottom of which the working electrode was placed with a circular area (diameter 1.5 cm) exposed to the unstirred electrolyte. A zinc current collector was clamped below the substrate. All potentials were measured versus a saturated calomel electrode. The counter-electrode was a titanium-based metallic grid placed parallel at ca. 2 cm above the disk.

2.2. Synthesis of patinas

Zinc substrates (Rhein-zink, > 99%) were grinded with SiC papers until grade P4000 with water lubricant and cleaned with ultrasound. Based on the work of Joo et al. [4], the simonkolleite layers were synthesized at -0.64 V (open circuit potential: -0.99 V) in 0.1 M

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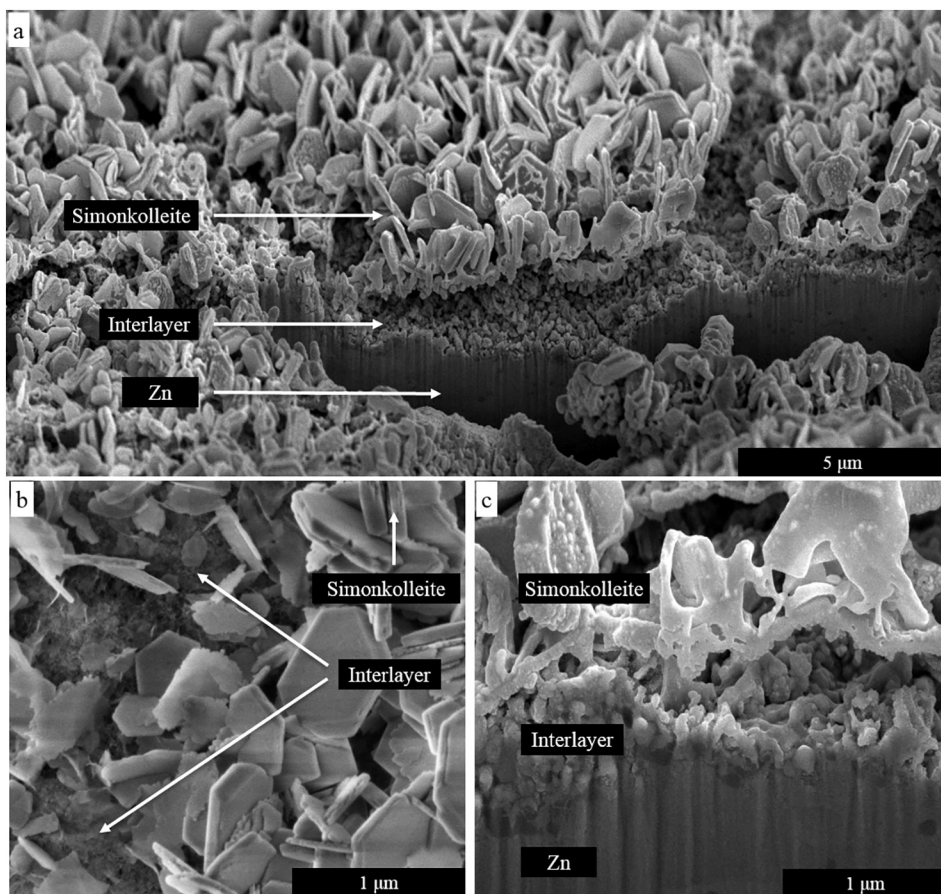


Fig. 1. FIB-SEM analysis of the patina. (a) Low-magnification tilted-view micrograph of the area around the FIB trench; (b) Top-view micrograph; (c) Zoom-in tilted-view micrograph at the trench edge.

NaCl dissolved in water:ethanol solution (1:1 volume ratio, pH = 6.2) for two hours. The resulting current was measured by chronoamperometry.

2.3. Study of cathodic polarization

The cathodic behaviours of zinc substrate with and without patina in Na_2SO_4 0.3 M (pH = 6.2) were compared. Linear sweep voltammetry (LSV, 1 mV/s) was used from open circuit potential (OCP) to -1.2 V at which an oxygen reduction current plateau was observed for zinc [18]. The current density was then monitored with chronoamperometry. The patina-covered samples were not dried between synthesis and cathodic polarization.

2.4. Crystalline phase and composition characterization

The CP were identified by Raman spectroscopy (Xplora Plus, Horiba) using a 532 nm laser source and a 1200 diffraction grating in static mode as well as in mapping mode ($15 \times 15 \mu\text{m}^2$ maps with $0.5 \mu\text{m}$ mesh). The crystalline structure was assessed by X-ray diffraction (XRD) with grazing-angle incidence (0.5°) and $\text{CuK}\alpha$ radiation (1.5408 \AA) and selective-area electron diffraction (SAED, see Section 2.5). Furthermore, the chemical composition of the surface was characterized by X-ray photoelectron spectroscopy (XPS) using $\text{Al-K}\alpha$ X-ray source (Thermo VG) and a cylindrical mirror analyser (RIBER) [19]. The C(1s) line of adventitious carbon at 284.8 eV binding energy was used to normalize the absolute binding energies. Auger electron spectra were measured to derive the α Auger parameter and differentiate zinc oxides, hydroxides and carbonates.

2.5. Electron microscopy analysis

Focused ion beam scanning electron microscopy (FIB-SEM) was used for high resolution imaging (FEI Helios NanoLab 600i, TLD, 2 kV). Transmission electron microscopy (TEM), SAED and high-angle annular dark-field transmission electron microscopy (HAADF-STEM) analyses were performed with a FEI Talos F200X apparatus equipped with Super-X EDX (energy dispersive X-ray spectroscopy) system. (S)TEM lamellae were prepared using FIB-SEM. A platinum layer was deposited on the samples using electron beam induced deposition to protect the surface from milling artefacts. CP porosity and pore sizes were evaluated based on micrograph analysis using the continuous phase size distribution method [10,13,20,21].

3. Results and discussion

During CP synthesis, after an initial phase of increase for several minutes, the current density remains relatively stable ($\sim 900\text{--}950 \mu\text{A}/\text{cm}^2$) until the end of the synthesis (not shown) suggesting the growing patina does not hinder the anodic process. On FIB-SEM micrographs, the patinas exhibit a two-layer microstructure (Fig. 1). The uppermost part is made of hexagonal nanosheets typical of simonkolleite regardless of the preparation method [4,7,22–28]. The nanosheet network (ca. $1\text{--}3 \mu\text{m}$ high, $20\text{--}100 \text{ nm}$ thin) exhibits a high porosity (60–80 vol%) with pore diameters around $300\text{--}600 \text{ nm}$ (but locally up to $2 \mu\text{m}$). This open structure is thus unlikely to act as a significant physical barrier to mass transport. The nanosheets are attached to a rough layer, thereafter named “interlayer”, located above the zinc substrate.

Characterization of the chemical composition and crystalline phase was first performed to identify the patina's constituents (Fig. 2). Raman microscopy analysis in static mode (Fig. 2a) shows the vibration peaks of simonkolleite ($393, 487, 733$ and 911 cm^{-1}) and ZnO (439 and

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