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Electrodeposition of nanocrystalline zinc on steel for enhanced resistance to corrosive wear

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ABSTRACT

In order to increase the resistance of electrogalvanized steel to corrosive wear, nanocrystalline zinc coating was electrodeposited onto the steel substrate using a sulfate bath with polyacrylamide as grain refiner. Corrosive wear tests were performed in a simulated seawater solution to evaluate the performance of the nanocrystalline zinc coating with its grain size around 40 nm, in comparison with that of coarse-grained zinc coating (grain size ~ 5 μm). It was demonstrated that material loss of the coarse-grained zinc coating was 39 times as large as that of the nanocrystalline one. The considerably higher corrosive wear resistance of the nanocrystalline zinc coating largely benefited from its increased mechanical strength due to nanocrystallization and higher surface activity, which improved the passivation capability with the formation of a more protective oxide scale. Detailed analyses were conducted to clarify the mechanism responsible for the improvements.

1. Introduction

Due to their more negative standard potential (−0.76 V vs. standard hydrogen electrode SHE) than iron (−0.44 V vs. SHE) [1], zinc coatings are often used to provide sacrificial cathodic protection for steel against corrosion even they are scratched or damaged. The lower cost and larger reserves of zinc, compared to other metals, as well as nontoxic and recyclable properties make it to be the most widely employed surface protective coating. According to the International Zinc Association, more than 5 million tons of zinc per year is used to protect steel against corrosion all over the world, and retrieves about 2.2 trillion USD annually from the capital lost for repair and replacement of corroded steel components [2]. The utilization of zinc coatings continuously increases with the increase in global demand for steel structures and others (such as energy-harvesting and storage cell) [3,4]. This also requires development of more protective zinc coatings and advanced coating processes. Nano-electrodeposition is one of such coating processes. Compared to conventional coarse-grained zinc coating, nanocrystalline zinc coating has demonstrated the following advantages: smoother and brighter surface, higher hardness, stronger corrosion resistance and improved tribological properties [5–14]. Besides, nano-electrodeposition technique is promising for industrialization, which can be achieved by adding additives in conventional electrolytes without post-treatment. Thus, electrodeposition of nano-zinc has become one of future directions for surface protection against corrosion.

Our earlier studies have demonstrated enhanced corrosion resistance of zinc coating as the grain size is reduced from micro-scale to nano-scale in simulated seawater (3.5 wt% NaCl solution), which is attributed to enhanced scale of corrosion products. Nano-Zn costing also shows higher dry sliding wear resistance, benefiting from increased hardness of nanocrystalline zinc coating [13,14]. Since in many applications, wear may occur in corrosive environments, it is importance to have a look at the behavior of the nano-Zn coating during corrosive wear and determine whether or not the improved surface scale of corrosion products may play a beneficial role in resisting synergistic attack involving corrosion and wear. This is the motivation for conducting this study on the resistance of nano-Zn coating to corrosive wear in a simulated seawater environment.

2. Experimental

2.1. Electrodeposition and characterization of zinc coatings

Nanocrystalline zinc coating was electrodeposited on carbon steel through galvanostatic current control using a basic sulfate bath ($ZnSO_4 \cdot 7H_2O$ 100 g L^{-1} and H_3BO_3 20 g L^{-1}) with added grain refiner (polyacrylamide 1 g L^{-1}). The optimization process of polyacrylamide concentrations is illustrated in Fig. S1. For comparison purpose, conventional coarse-grained zinc coating was also electrodeposited using the basic sulfate bath. The pH of the baths was maintained at 1–2, and the current density was 3 A dm^{-2} with electrodeposition time of 1 h at room temperature (25 ± 1 °C) for all experiments. A detailed description of the bath configuration procedure and operating conditions can

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be found in reference [14,15]. Variations in potential with the electrodeposition time of zinc coatings in different baths were analyzed by chronopotentiometry test. All the electrochemical experiments were performed at room temperature in a conventional three electrode cell by Gamry electrochemical workstation with platinum plate, saturated calomel electrode (SCE) and glassy carbon electrode as the auxiliary, reference and working electrode, respectively. Prior to each experiment, the glassy carbon electrode was polished with an aqueous slurry of 0.05 μm alumina, rinsed with deionized water, and then dried with N_2.

After electrodeposition, zinc coatings were rinsed immediately in deionized water and dried, followed by structure characterization and property evaluation. Grain size and cross-sectional morphology of zinc coatings were characterized by transmission electron microscopy (TEM, JEM-2100), scanning electron microscopy (SEM, Helios Nanolab 600i) and energy dispersive X-ray spectroscopy (EDS). The surface morphology, roughness, electron work function, elastic modulus, deformation, adhesive force of zinc coatings were characterized using a multimode atomic force microscope with a nano-Kelvin Probe (MAFM, Brucker Multimode 8). Through the collection of variations in contact potential between the probe and the sample surfaces by the nano Kelvin Probe in AFM, the in situ AFM analysis reflects changes in properties of the coatings before and after corrosive wear. Both of electron work function and mechanical properties (modulus, deformation and adhesion magnitude) of the samples are proportional to their contact potentials. Detailed discussion on the relationships between the contact potential and the coating properties is given in Supplementary information.

2.2. Corrosive wear testing

Corrosive wear tests were performed for the Zn coatings using a pin-on-disc tribometer (Neuchatel, CSEM Instruments CH-2007) with a container, in which simulated seawater was used as a corrosive medium. The disc was the coating and the pin was a SiN ball with a diameter of 6 mm. All tests were performed at a sliding speed of 0.05 cm s^{-1} along a circle path of 2 mm in diameter under a load of 1 N for 1 h. The tests were carried at the room temperature with a relative humidity of approximately 50%. During the wear tests, friction coefficient curves were also recorded. Wear scars were analyzed using a ZeGage 3D optical profiler, from which the volume loss was determined by measuring the cross-sectional area of wear scar and then integrating it over the entire wear track. This calculation can be conducted automatically with the ZeGage's software. The surface morphology, element composition, electron work function and mechanical property of the wear scars were analyzed using SEM, EDS and MAFM.

3. Results and discussion

3.1. Electrodeposition of zinc coatings

Fig. 1 shows the AFM morphologies of coarse-grained and nanocrystalline zinc coatings electrodeposited using the basic sulfate bath without or with the grain refiner under the same deposition conditions. As shown, the coarse-grained zinc coating has an irregular crystallite size distribution (around 5 μm, Fig. 1a) and its surface is rough (Ra = 306 nm, Fig. 1b), while the nanocrystalline zinc coating shows a uniform, fine and dense grain distribution (less than 100 nm, Fig. 1c) and its surface is much smooth (Ra = 1.3 nm, Fig. 1d). Fig. 2 illustrates a TEM image of the nanocrystalline Zn coating (the dark domains in the TEM image are nanocrystalline zinc.), showing that the average grain size is approximately 40 nm. The thicknesses of coarse-grained and nanocrystalline zinc coatings are about 43 and 38 μm, respectively

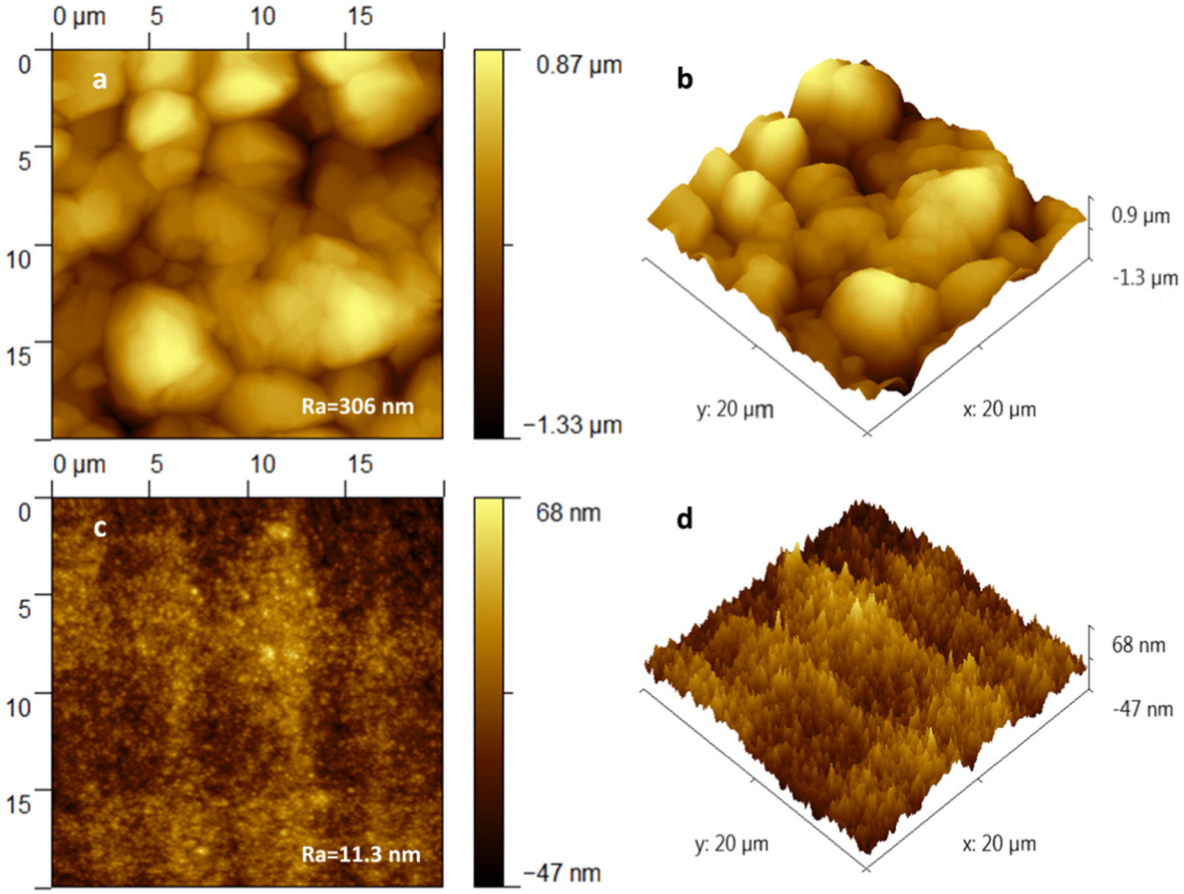

Fig. 1. AFM micrographs of coarse-grained (a, b) and nanocrystalline (c, d) zinc coatings.