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Challenges and strategies of surface modification of electrogalvanized coatings for electron microscopy analysis

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ABSTRACT

Despite wide usage of electrogalvanized coatings in various applications, characterization studies on their micro/crystal structure, and the understanding of how they correspondingly affect the properties, such as corrosion, are rather limited. This is mainly attributed to some difficulties in preparing and examining the zinc coating layers, owing to their intrinsically low corrosion resistance and refined nano-scaled crystallite size. This study aims to examine such challenges systematically and propose some mitigation strategies. Particularly, sample preparation processes, including surface finishing for metallography and sample thinning processes are explored. Furthermore, a range of electron microscopy techniques, including scanning electron microscopy (SEM), electron back scattered diffractometry (EBSD), and transmission electron microscopy (TEM) are investigated in relation to the achievable clarity of microstructural details of electrogalvanized coatings.

1. Introduction

Owing to good corrosion protection at moderate cost, ductility and formability, and a uniformly thin coating layer of electrodeposited zinc, also termed electrogalvanized coating, has been widely employed as a surface finish in various industrial applications, ranging from automotives, electronics, and households (Wilcox and Gabe, 1993; Marder, 2000; Muster and Cole, 2004; Crotty, 1996). The esteemed properties primarily result from chemistry of zinc and the coating's microstructure and crystallographic structure of coating (Ramanauskas et al., 1997; Morales et al., 2007; Chianpairot et al., 2011; Yoshioka et al., 1990; Winand, 1991; Eppensteiner and Jennkind, 2007; Zhang et al., 2005; Ramanauskas et al., 2007). While understanding its structure would provide effective channels to tailor and enhance the properties of electrogalvanized coating, in a major part, this is barred by delicate nature of metallic zinc with respect to surface preparation protocols required for microscopy examinations. This is evidenced by the presence of a very limited number of publications devoted to metallographic studies of electrogalvanized coating (Raeissi et al., 2007; Wang et al., 2006) and consistent remarks on difficulties during sample preparation, including rapid surface oxidation, peel-off, and non-uniformity upon cutting, grinding, and surface polishing (Injeti and Leo, 2008; Zhang et al., 2014). Furthermore, the challenge is often escalated by a refinement of the coating structure in a nanometer scale, which necessitates distinguished surface preparation quality for advanced microscopy characterizations (Saber et al., 2003; Muralidhara and Arthoba Naik, 2008).

In the present study, surface preparation of the electrogalvanized coatings for advanced microscopy techniques, including field-emission electron microscopy (FE-SEM), electron back scattered diffractometry (EBSD), and transmission electron microscopy (TEM) are systematically examined. Particularly, the challenges encountered upon sample preparations for these techniques are deduced and corresponding strategies, including electropolishing, to mitigate the problems are proposed and investigated. Optimal outcomes obtained with the current study would specifically provide proper methodology for the electron microscopy of electrogalvanized coatings, and also shed some lights on possible surface preparation protocols for other types of galvanized and readily-oxidized coatings.

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2. Surface preparation and characterization: challenge and strategies

2.1. Surface finishing for metallography

Two of the common techniques for examination of microstructural details of metal surfaces are scanning electron microscopy (SEM) and electron back scattered diffractometry (EBSD). While these two techniques commonly require highly planar and uniform conditions for the surface of the sample, there are some distinctive requirements which pertain to the usage and functions of the techniques, as follows:

2.1.1. SEM

Through the scanning of secondary or back-scattered electrons on interested areas, the SEM is commonly employed for analyzing the morphology and topography of materials in the scale of a few microns to nanometer. Three electron sources of the SEM, including tungsten-filament, LaB_6-crystal, and field-emission, are available, with the latter, also termed FE-SEM, providing the highest resolution (Exner and Weinbruch, 2004). Grain structure, granules, roughness, thickness, and cracks are among possible microstructural features of the electrogalvanized coating to be examined under the SEM.

Nevertheless, some basic challenges exist in its surface preparation process, which consists of (1) sample cutting, (2) mounting, (3) grinding, (4) polishing, and (5) etching (Aliya, 2004). Due to the intrinsic sacrificial nature of electrogalvanized coating, the major issues being faced are developments of surface non-uniformity in the polishing step and localized corrosion attack induced by chemical etchants of the last step which hinders visibility of the microstructural features. Whereas the first problem is commonly mitigated by using oil-based lubricants as polishing mediums (Samuels, 2003), the best practice for the latter issue remains unclear.

In the present study, 3 strategies to prepare the surface of electrogalvanized coating for microstructural examination under SEM were examined comparatively, including polishing with oil-based diamond suspension, final polishing with water based colloidal silica solution, and electropolishing with Spyridelis method. Whereas colloidal silica is a common polishing medium for Al, Cu, and Fe and exhibits mild etchant character, Spyridelis method which employs phosphoric acid in ethyl alcohol, has been adopted to etch thin sheets of zinc (Spyridelis, 1971).

2.1.2. EBSD

EBSD is the advanced technique for characterization of crystal orientations of a crystalline or polycrystalline material. Equipped in SEM, EBSD analyzes diffraction pattern generated from backscattered portion of electron beams and develops orientation mapping representing individual crystallographic planes that are present on materials' surfaces (Venables and Harland, 1973). To prepare samples for the EBSD analysis, perfectly clear and highly smooth surface, somewhat exceeding the tolerable quality of SEM samples, is required. Such challenge in sample preparation may therefore partly explain a very limited number of crystallographic studies of galvanized coatings.

For the most parts, the EBSD samples are prepared with the same steps as those for SEM samples, except that higher attention is to be paid on the uniformity and defect-free quality of the surface following polishing. Furthermore, minimally etched surface quality is merely needed. If structures of a substrate or a coating interface are to be characterized in concurrent to the coating, it is also important to control and balance the polishing and etching rates of the adjoined materials. Such process is often found difficult due to a relatively rapid polishing rate of metallic zinc.

In the present study, 2 strategies to prepare the surface of electrogalvanized coating for crystal structure examination with the EBSD were investigated, namely final polishing with water-based colloidal silica solution, and electropolishing with Adair method which employed perchloric acid in ethanol (Edington, 1975). These two methods were chosen as it was known that they could also polish the surface of steel substrates (Weidmann, 1985).

2.2. Sample thinning for TEM

TEM is the important characterizing technique for analyzing the microstructure and crystal structure of materials in the nanometer and angstrom regimes. Bright field mode allows analysis of grain structure and atomic arrangement, whereas the diffraction mode provides crystal orientations and observations of defects. Despite its powerful functions, TEM is known to be one of the hardest microscopy techniques to prepare a sample. Particularly, the sample needs to be thinned below 50–60 nm to allow electron to transmit through. Mechanical dimpling, ion milling, and electrochemical polishing are among possible processes to prepare exceptionally thin samples (Reimer, 2013)

Similar to EBSD, TEM studies of electrogalvanized coatings are very limited. Furthermore, a specific guideline for TEM sample preparation of the zinc-based coating is not available in publications. Spyridelis and Adair electrochemical polishing methods were comparatively chosen for examination herein with respect to clarity of TEM micrographs and corresponding diffraction patterns.

3. Experimental

3.1. Sample fabrication

A set of electrogalvanized specimens was prepared by the electrodeposition process using the environmentally friendly alkaline non-cyanide bath (Injeti and Leo, 2008). The plating bath contained 10 g/l Zn and 120 g/l NaOH and some commercial brighteners and levelers (Pushpavanam, 2006). Low carbon steel ($25 \times 50 \times 1$ mm) was used as substrates, countered by platinum mesh anodes upon deposition. Prior to plating, the samples were soak-cleaned in a 50 °C 50% NaOH solution for 30 mins, electro-cleaned in 5% NaOH at room temperature for another 10 s, and finally dipped in 5% HCl for 10 s. Electrodeposition was carried out at the room temperature using a current density of 2 A/dm^2 for 30 mins. Subsequently, the samples were cleaned, dried, and mounted in one of the configurations (30 mm O.D.) as presented in Fig. 1 ready for the different surface preparation protocols and characterization techniques. As for the sandwich-mounted samples (Chu and Sheng, 1984), the preparation steps include coupling 2 cross-sectioned samples with their coating layers facing one another, inserting the couple in a copper tube (3 mm O.D.), filling of Gatan glue in the tube, cutting of the specimen to a 200 μm disc, and grinding the disc down to 100 μm.

3.2. Test protocols

3.2.1. Surface preparation

The cross-sectioned samples that were cold mounted were prepared for the SEM specimens by grinding on a rotating disc with abrasive SiC papers with 800–4000 grits and polishing by 1 of the 3 schemes, namely (1) mechanical polishing with an oil-based diamond suspension (3 μm and 1 μm) on a rotating disc, (2) final polishing with a 50% colloidal silica (0.05 μm) slurry in a 50 Hz vibration polishing machine, and (3) final polishing with electrochemical polishing using the Spyridelis' formulation composed of 50% orthophosphoric acid in ethyl alcohol with 3 V and current density of 2 A/dm^2 at room temperature for 5–20 s (Spyridelis,