Chapter 1

Introduction

Summary

Zn-Al-Mg coatings have attracted in recent years a lot of attention owing to their excellent corrosion resistance. Nevertheless, the high cracking tendency, as a long-lasting drawback and challenge of these thin coatings, limits their formability performance. This less-understood aspect essentially demands a fundamental comprehension about the origin and mechanism of cracking in these coatings. In this general introductory chapter, Zn-Al-Mg coatings which are typically produced via a hot-dip galvanizing process on steel substrates are introduced. The general background, approach and motivation are incorporated in order to shed light on the aims and direction of the present thesis.
1.1 Phenomenology of cracking

Cracking is a ubiquitous phenomenon in nature that takes its root and meaning from the sound that it usually makes [1]. In the ontological sense, cracking is the manifestation of imperfection and division in the orderly and complete mode of beings (or the ideal Platonic forms). The artwork of M. C. Escher entitled Contrast (Order and Chaos) depicted in Figure 1.1, beautifully illustrates the apparent chaotic nature of cracking and fracture in different solid-state materials, encircling an orderly crack-free object. In the epistemological sense, the phenomenon of cracking can be the object of inquiry by an observer (i.e. the subject) through systematic measurement of its attributes as first introduced by René Descartes who based the modern scientific method in 1637 [2]. In the physical sense, a crack is formed through a dynamic process as a result of an internal or external stimulus. The phenomenon of cracking, vis-à-vis its origin and mechanism, can be traced back from atomic structure/arrangement and microstructural features to the stress/strain condition of the examined material at the continuum micro/macro level. Overcoming multi-scale cracks in structural materials is a challenging objective that requires a fundamental understanding via natural sciences, specifically materials science and mechanics of materials disciplines. The present thesis is an attempt to tackle and overcome this challenge in Zn-Al-Mg coating materials.

Figure 1.1 Contrast (Order and Chaos), a lithograph by the artist M. C. Escher, 1950. Reproduced by the Copyright permission from M. C. Escher Foundation.
1.2 Zinc-based and Zn-Al-Mg coatings

Zinc-based thin films and coatings are distinguished classes of engineering materials that are widely utilized owing to their exceptional anti-corrosion properties, biocompatibility and natural abundance [3–6]. Zinc-coated steel sheets are amongst the important materials for various applications, particularly in the automotive, construction and household appliance industries [7–9]. Zinc and zinc-alloy coatings provide corrosion resistance for steels by a process of sacrificial cathodic protection (i.e. galvanic protection) and/or the formation of passive by-products acting as a barrier to electrochemical reaction (i.e. barrier protection) [10–12]. These coatings exhibit a thickness of around 10-15 µm and are primarily produced by the hot-dip galvanization (HDG) process or by the more energy-consuming electro-galvanizing processes. In the latest years corrosion resistance of such coatings has been significantly improved by alloying the HDG bath with moderate amounts of elements such as aluminum and magnesium [4]. Mg addition is particularly desirable, since it enhances corrosion resistance by promoting the formation of a more stable corrosion barrier layer [13]. In addition, the resultant higher coating hardness resolves issues of galling during forming processes. Therefore, Zn-Al-Mg alloy coatings offer excellent corrosion resistance and anti-galling performance for the underlying steel substrates as explored in various studies in the literature [8,9,14–18]. Moreover, ZnAlMg-based coatings require only half the thickness of pure zinc (GI) coatings for an equivalent or even better corrosion protection. This significantly saves resources and reduces production costs.

Nonetheless, Mg-alloyed zinc coatings especially Zn-Al-Mg coatings suffer from high cracking tendency once subjected to deformation and forming processes [19–21]. Furthermore, the formability of these coatings is considerably limited due to the prevalent cracking as their main drawback [19,22]. This is especially seen when Zn-Al-Mg coated panels are stacked under conditions of high humidity for a long time. The generated cracks with a large opening on the surface enable penetration of corrosive media into the coating and consequently can facilitate the corrosion of the steel substrates. Thus, it is crucial to avoid such detrimental cracks in these coatings.

1.3 Hot-dip galvanization (HDG) process

Hot-dip galvanization is the process of coating fabricated steel by immersing it in a bath of zinc or zinc alloys (e.g. Zn-Al-Mg). Zinc has been used by mankind from the ancient times and antiquity. Yet, the invention of the HDG procedure goes back to 1742 when Paul Jacques Malouin described this technique in a presentation [23]. The galvanization is mainly performed through two different methods, namely batch galvanizing and continuous galvanizing [24]. The latter method is the dominant way
of galvanizing nowadays, due to its high efficiency and economic advantages. The schematic representation of the continuous HDG process is given in Figure 1.2. In this process, a steel strip is initially subjected to pre-dip cleaning and pre-annealing depending on the steel type around 700 °C to 760 °C (above the recrystallization temperature). These steps are essential to remove the contamination and ensure a good adhesion between the coating and the steel substrate. Prior to dipping, the moistures of the clean steel strip are removed to prevent oxidation during the process. The steel strip is usually cooled down to 460 °C before the immersion into the molten zinc/zinc alloy bath. The steel strip is consequently coated in the molten bath and pass through post-dipping stages such as heat treatment. There are several parameters that can be controlled in this process including bath temperature (mainly set around 460 °C), dipping time, strip entry temperature, strip entry speed and gas volume for the wiping stage [5,24].

Figure 1.2 Schematic representation of the continuous hot-dip galvanization process for fabrication of Zn-based coatings on steel substrates [24].

1.4 Problem definition, aims and approach

In spite of the excellent corrosion resistance, hot-dip galvanized Zn-Al-Mg coatings currently exhibit very low cracking tolerance. This research is driven by the desire of the steel industry and its countless end-users to improve the cracking resistance and formability of Zn-Al-Mg coated steels. These are among the most promising coated steels in terms of their corrosion resistance and high strength; however, their widespread application is limited by formability issues. This research will remove these barriers by providing an in-depth understanding of how the cracking behavior of Zn-Al-Mg coatings is influenced by the hot-dip galvanization process, the chemical composition and the microstructure of the coatings. Therefore,
the principal aims of this thesis are to (1) fundamentally understand the origin and mechanisms of cracking in Zn-Al-Mg coatings and (2) accordingly overcome and resolve the cracking and formability issues associated with these coatings through optimizing material and process design. To achieve these objectives, this thesis offers a comprehensive bottom-to-up and multi-aspect approach unraveling the atomic structure, nanoscale features and defects, microstructural characteristics, crystallographic orientation/texture, micro-macro stress/strain mapping, cracking origin and mechanism, etc. utilizing advanced correlative microscopy characterization and in-situ mechanical testing techniques. The graphical abstract shown in Figure 1.3 provides an overview of the present thesis, emphasizing the structure-properties relationship across length scales, linking the atomic structure to Zn-Al-Mg coated steel rolls in meter scale. In particular, this thesis correlates the structure of Zn-Al-Mg coatings to the associated mechanical and formability properties through theoretical, numerical and experimental approaches. In addition to the scientific understanding, one of the significant motivations of this thesis is to provide practical strategies and solutions to solve the long-lasting cracking problem of these coatings. In the light of the findings and solutions accomplished in this thesis, next-generation highly formable and durable Zn-Al-Mg coatings are aimed to be optimized and developed.

Figure 1.3 Graphical abstract indicating the multi-scale and comprehensive approach of the present thesis.
1.5 Outline of the thesis

In order to systematically address the above objectives, stepwise and dedicated research studies have been performed. Accordingly, in addition to this introductory chapter, the present thesis is divided into the following chapters:

- A literature review focusing on the Zn-Al-Mg coatings family is presented in Chapter 2. It covers the previous studies on microstructural features and mechanical behavior of ZnAlMg coatings. The deformation mechanisms in hexagonal close-packed (HCP) zinc alloys are incorporated. The state of the art in the field of galvanized Zn-Al-Mg coatings has been included in this chapter. Finally, the deficiencies and the knowledge gap in this field are discussed.

- The genesis and mechanism of micro-scale deformation and cracking in Zn-Al-Mg coatings are provided in Chapter 3. A (patented) quantitative methodology is developed based on the micromechanical properties and crystallographic orientation in order to predict cracking during deformation. The role of the crystallographic orientation of the grains in the cracking tendency is elucidated. The results of the in-depth microstructural characterization, nanoindentation tests, in-situ scanning electron microscopy (SEM) tensile/bending tests, finite element analysis (FEA), ex-situ and in-situ orientation image microscopy (OIM) analyses are provided and discussed in this chapter. In particular, this chapter lays a foundation for the next following chapters by identifying and elucidating the detrimental factors for the cracking resistance and formability of these coatings.

- Chapter 4 provides a key step towards realizing crack-resistant and formable Zn-Al-Mg coatings on steel substrates. In this chapter, the microstructure of the coating is tailored by eliminating the detrimental component (i.e. binary eutectic) and a highly ductile and tough coating is developed as a consequence. This chapter entails the major theoretical elucidations of the present thesis. Furthermore, it opens a gateway towards designing crack-resistant coating microstructure, which is of significant practical importance. High-end scanning transmission electron microscopy is utilized to capture the nano-scale defects in this chapter. Quantitative dislocation density, slip trace analysis, Taylor factor, grain boundary slip transfer and geometrically necessary dislocation (GND) calculations are integrated in the analysis to correlate the microstructure to plastic deformation.
The understanding of cracking behavior and formability of Zn-Al-Mg coatings are expanded by investigating the effect of the steel substrates in Chapter 5. This chapter signifies the importance of the steel substrate type for the mechanical performance of Zn-Al-Mg coated steels as a whole system. Explicitly, Zn-Al-Mg coatings on high strength low-alloy (HSLA) steel and interstitial free (IF) steel types are studied. The deformation behavior of the steel substrates are linked to the cracking behavior of the coatings. In this chapter, strain mapping by digital image correlation technique is conducted on the coated steel specimens across length scales.

Chapter 6 unfolds remarkable cracking resistance and formability properties obtained by applying crystallographic texture control on Zn-Al-Mg coatings. It is shown in this chapter that the simultaneous microstructure and crystallographic texture control can result in superb formability in Mg-alloyed zinc coating. The methodology developed in Chapter 3 is applied in this chapter and it has been further confirmed that the method is capable of predicting/explaining the cracking tendency of Zn-Al-Mg coatings.

Chapter 7 is dedicated to explore the influence of grain refinement on the deformation and cracking resistance in Zn-Al-Mg coatings. To this end, two ranges of grain sizes in the microstructures of the coatings are attained and studied. This chapter shows that the cracking behavior and deformation mechanism of these coatings are grain size-dependent. These facts are revealed by performing in-situ SEM tensile tests and electron backscatter diffraction (EBSD) analyses.

In Chapter 8, a summary of the contents of the thesis is provided. It also gives a prospective outlook of possible future research works on Zn-Al-Mg coatings in accordance with the approach, findings and methodology developed in this thesis.
References


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