



The influence of microstructure on surface phenomena: Rolled zinc

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Abstract

A series of rolled zinc (Zn) alloys, all with purity exceeding 99.7%, have been shown to have material losses due to corrosion spanning an order of magnitude during field exposure trials. In order to explain these large variations in corrosion performance, the influence of alloying additions and microstructure has been investigated. Corrosion rates were found to increase with increasing alloying additions of copper (Cu) and, depending upon its distribution, titanium (Ti). The influence of grain size was investigated using a series of heat-treated rolled zinc specimens. Binary Zn–Ti and Zn–Cu alloys were used to study the independent influences of Ti and Cu on zinc corrosion. An increased understanding of the influence of Cu:Ti ratios has been developed and an approach to optimise the corrosion resistance of rolled zinc materials has been proposed.

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1. Introduction

Zinc in rolled form finds use as roof sheeting, battery cans and for more specialised uses such as photoengraving surfaces [1]. Also, due to zinc's extensive use in the galvanic protection of steel, Zn sheet is commonly used as a standard reference material by corrosion

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scientists to assess the corrosivity of global environments. However, experience within our workplace over the last 15 years has shown that rolled zincs, whilst exhibiting a purity of greater than 99%, can display significant variations in their corrosion performance [2–4].

At present, the desired mechanical properties of rolled Zn are generally achieved through the alloying additions of Cu and Ti at levels of 0.1–0.2% [5]. Cu additions up to approximately 1% exist in solid solution with Zn, and result in higher strength, hardness and creep resistance, and higher recrystallisation temperatures. In contrast, the lower solubility of Ti (up to 0.11%) results in the precipitation of a Zn-rich intermetallic phase with a composition of TiZn_{15} [6]. This intermetallic phase acts to decrease the grain size of cast Zn and to restrain grain growth in rolled Zn at elevated temperatures. Ti is reported to have little effect on the tensile strength and hardness of rolled Zn, but does increase creep resistance, particularly when added in combination with Cu [6]. In addition to the TiZn_{15} phase, Du Val–Benoit [7] found that the slow solidification of Zn–Cu–Ti alloys (0.2–2.5% Cu, 0.1% Ti) can form other secondary phases. These compounds are reported to be hard, and harmful to the ductility of the alloys. One suggested composition for such an intermetallic phase is Zn 89%, Cu 8.2% and Ti 3.1%. However, current Zn–Cu–Ti ternary phase diagrams suggest that Cu and Ti, at the levels used for rolled Zn production, do not form mixed ternary phases [8].

While a considerable body of literature exists on the microstructural effects for other metals (i.e. aluminium [9,10], magnesium [11] and stainless steel [12]), particularly those alloys with high fractions of second phase particles (i.e. aluminium), the literature on microstructural effects for Zn or galvanised steel is less extensive.

Historically, work on Zn has focussed on grain boundary effects. Work by Sergei et al. [13] and Abayarathna et al. [14] on the corrosion of single Zn crystals highlighted the role of grain orientation. These authors found that the development of oxides of high continuity resulted in decreased corrosion on (0001) crystallographic planes. Tsuru et al. [15] found that individual grains may show different potentials when exposed to acidic solutions. In multicrystalline material, Powers [16] demonstrated that anodic dissolution starts preferentially at grain boundaries. Dikse [17] demonstrated that fine-grained structures are less susceptible to corrosion than coarse-grained structures.

More recent work has further investigated the link between microstructural features (and some compositional differences), corrosion susceptibility, and the properties of resulting oxides. Ramanauskas et al. [18] investigated the corrosion performance of electrodeposited Zn, Zn–Co (0.6%), Zn–Ni (12%) and Zn–Fe (0.4%) alloys in 0.1 M NaCl/0.1 M NaHCO_3 solutions. The corrosion performance was compared before and after annealing in air at 225 °C for 8 h. Only the Zn–Ni alloy showed appreciable differences in performance (increased corrosion current) as a result of the annealing. The authors argue that annealing leads to a more ordered metallic structure, and that a less ordered structure has an increased surface activity for oxide formation. That is, a less ordered structure favours the formation of hydrated $\text{Zn(OH)}_2\text{:ZnO}$ layers that are thought to have an increased current resistance compared to ZnO, which is the favoured oxide formed on more ordered structures. Similar effects were noted by Arenas et al. [19], who studied the effect of ion implantation of rare earths into galvanised steel. These authors noted a significant improvement in corrosion resistance, which they attributed to the development of oxides with greater charge transfer resistance (there were no evident compositional differences in oxides formed with and without ion implementation).

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