Review

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Sacrificial Zn–Ni coatings by electroplating and hydrogen embrittlement of high-strength steels

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Abstract: A review of sacrificial Zn–Ni electroplating coatings on high-strength steels is presented. These steels are used for heavy structural applications such as landing gears, etc., that are subjected to high stresses and corrosive environments in service. The electroplating process involving aqueous electrolytes invariably produces hydrogen. The emitted hydrogen can diffuse into substrate steel, contributing to the delayed failures by hydrogen embrittlement. Microstructural inhomogeneities arising from the heat treatments and defects produced during coatings and those inherently present in the steels can trap hydrogen emitted during plating. Dissolved and trapped hydrogen can slowly diffuse to the stress concentrations or crack tips, contributing to the delayed structural failures. Baking after plating helps to eliminate hydrogen to some extent, though it may introduce some thermomechanical stresses at the bimaterial interfaces. This review discusses a) the current state of sacrificial Zn–Ni coatings, b) their protection against corrosion of the substrate, c) the associated hydrogen embrittlement predominately under cyclic loads, and d) recent advances in terms of the compositionally modulated coatings for enhanced protection.

Keywords: electroplating; high strength steels; hydrogen embrittlement; Zn–Ni coatings.

1 Introduction

High-strength steels are used in several industries, including construction, oil and gas, energy, automotive, and aerospace structures. For example, most modern

aerospace structural components—like fasteners and main landing gears—involve low-alloy and high-strength steels. They are durable and tough enough to meet or exceed minimum application requirements. These alloys have good mechanical properties, including yield and ultimate tensile strengths. During use, many of them are subjected to cyclic loads and corrosive environments, and even more so when working in naval environments. De-icing, for example, results in aqueous environments containing corrosive salts that can contribute to stress corrosion crack initiation and growth under cyclic loads. Sacrificial protective coatings are therefore used to extend the life of these components (Harvey 1930).

Figure 1 shows the early work on the fatigue life of Zn-plated steels for structural applications by Swanger and France (1932) at the National Bureau of Standards. Zinc was used as a sacrificial coating on steels to protect them from corrosive environments encountered in service. Zinc coatings were applied by pickling, galvanizing, or electroplating to evaluate their performance in relation to the bare, uncoated steel substrate. Figure 1 clearly shows that the electroplating of Zn enhances the fatigue life of the steel. In addition to zinc and cadmium has been used as a protective coating for the high-strength steels used in fasteners (Baldwin and Smith 1996). Cadmium was found to provide excellent corrosion protection from saltwater containing NaCl and other kinds of salts, as diffusion rates of hydrogen in Cd are low. It is also relatively inexpensive, with a low coefficient of friction needed for fasteners. Unlike the Zn coating, the Cd coating finish-luster does not quickly tarnish or fade. However, the significant problem with cadmium plating is the cyanide rinse used during the plating process (ASM Handbook, Mooney 2005).

Most industrialized countries have entirely banned cadmium plating due to cyanide poisoning, except for rare applications. There have been significant efforts, funded particularly by the US government in small business initiatives research (SBIR), to develop Zn–Ni electroplated coatings, Brown NAVAIR and Berman Airforce (2011) and NAVY-US Airforce (2012). It is being developed as an alternative to Cd plating to protect the high-strength steels used in many industrial applications. There are many other

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Figure 1: (A) Effect of Zn plating on the fatigue life of a steel substrate. (B) Comparison of axial versus rotating fatigue lives with and without coatings. From Swanger and France (1932).

independent research efforts at major universities to develop better coatings. Most of the results are available in the open literature, including an early review of the electroplated Zn–Ni coatings on steels (Hall 1983). While the research efforts are continuing, most recent efforts to improve the coatings are concentrated on evaluating the corrosion resistance of the electroplated coatings and not much on the fatigue life in a corrosive environment. Some efforts have been made to evaluate their susceptibility to hydrogen embrittlement using slow strain rate tests.

The major concern during electroplating of high-strength steels is the associated hydrogen generation, absorption, and diffusion into the substrate steels that are intrinsically prone to hydrogen embrittlement due to their high strength. The development of the coatings intimately involves an understanding of the sacrificial protection against corrosion during service. In addition, it involves the containment of the hydrogen embrittlement of the substrate. The hydrogen embrittlement contributes to delayed failures of the electroplated components, particularly under cyclic loads encountered during service. The problem gets compounded due to the presence of hydrogen traps. These are inherently present due to microstructural modifications introduced during the heat treatment of the steels, which are required to obtain the optimum strength needed for service applications. In addition, residual stresses are introduced either intentionally—as in the case of shot peening the steel before plating—or by the plating itself, predominately due to lattice parameter mismatch at the plating-substrate interface.

Thus, the development of proper sacrificial electroplating protection for the high-strength steels involves several disciplines covering electrochemistry on one side,

material science, and mechanics on the other. There have been many short reviews of this subject covering various aspects. Here, we present the current state of understanding of electroplated sacrificial coatings for high-strength steels, covering the research developments of this area and the avenues for further research needed for the improved sacrificial coatings for service applications. Some of the Navy-sponsored programs involve relative evaluation of industrially-developed or provided coating processes. Our emphasis here is mainly on understanding the process for future development based on the available data rather than any endorsement of a particular process.

2 Background

2.1 Electrochemical nature of aqueous corrosion

The corrosion of steel can be viewed as a natural electrochemical process in the presence of any environment containing moisture and oxygen. It slowly destroys the integrity of the metal structures under load. The electrochemical process, in short, involves two electrode reactions that can occur spontaneously at the interface between the metal and the aqueous environment, depending on the Gibbs-free energy of the system. One is the anodic-oxidation reaction of the metal discharging electrons from the metal substrate. The other is the cathodic-reduction reaction that restores the electron deficiency at the metal surface. The exchange of electrons between anodic and cathodic reactions causes electronic current flow across the metal interface and is

called electrode corrosion potential, E_{corr} . Hydrogen emission during the anodic–cathodic reactions, which can subsequently embrittle the steel, is an unavoidable byproduct of these reactions. Baking helps remove the dissolved hydrogen to some extent (Evans 1992).

In the case of sacrificial coatings of high-strength steels, the protective coating of steels involves sacrificing the coating in preference to the substrate steel during the service. Understanding the sacrificial electroplating coatings for high-strength steels requires some knowledge of electrochemistry, material science, and mechanics (Fontana 2005). In this review, all these aspects are covered to the extent required for our understanding.

Figure 1 provides the early work on the effect of Zn electroplating on fatigue life, Swanger and France (1932). Figure 1(A) shows that zinc electroplating has significantly improved the fatigue life of the tempered carbon steel. Fatigue life evaluations after the coating are typically done using a rotating bending machine with the load ratio, $R = -1$, as it is easier to set up. However, material response under cyclic loads can differ if the loads are applied axially, as shown in Figure 1(B). Figure 1(B) shows that the fatigue strength can be much lower in axial fatigue due to the accentuated crack initiation and growth processes and/or hydrogen embrittlement due to enhanced diffusion kinetics. The implication is that the test conditions are to be noted while comparing the results from different data sets.

Electroplating involves anodic and cathodic reactions taking place simultaneously that involve hydrogen and hydroxyl ions contributing to electrical conductivity. Figure 2 schematically summarizes the electrochemical reactions that can occur, for example, on an iron substrate in an aqueous electrolyte (Gordon 2005). An electrochemical cell is formed when a potential is applied across the specimen. In an acidic electrolyte, the iron can disassociate by anodic reactions at localized regions. There are two reactions possible for Fe, as given below.

Of the two, the electrode potential for the first one is slightly more negative compared to the Cd reaction involving $\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$, while the second one is highly positive. Because Cd is used as a sacrificial coating, we can speculate that reaction 2 above may be overwhelming. The point, however, is that the anodic reaction involves an electron emission that sets the electrical charges, as noted in Figure 2.

Several possible cathodic reactions can occur along the surface of the specimen, as illustrated in the figure. Most importantly, there is hydrogen generation that can

diffuse into either the metal or the electrolyte. Movement of ions in the liquid or movement of electrons in the metal results in associated current flow, as in any electrochemical cell.

As a sacrificial coating, zinc protects the steel by corroding first in preference over the steel substrate. The cathodic and anodic reactions can be understood using the polarization curves. Thermodynamics explains the energy changes providing the driving force and controlling the direction for a chemical reaction. The kinetics of the reaction, however, depends on other factors. For example, in an HCl acidic solution, the reaction of Zn with HCl is characterized by the chemical reaction shown below, resulting in a dynamic equilibrium:

In electrolyte, this can be represented in ionic form as:

Eliminating Cl^- from both sides of the reaction gives:

Reaction 5 can be separated as follows:

All corrosion reactions in water involve anodic reactions similar to reaction 6 above. In general, for corroding metals, the anodic reaction can be represented in the form:

Cathodic reactions are few. The simplest and most common one is the reduction of hydrogen ions in acid solution (reaction 7). The reduction of dissolved oxygen is

Electro Chemical Process Involved in Electro Plating

Figure 2: Electrochemical cell between anodic and cathodic regions on the steel surface.

often observed in neutral and acid solutions exposed to ambient air. The respective reduction reactions are:

And:

In the absence of all other reduction reactions, water will be reduced by:

It is equivalent to reaction 7, assuming dissociation of water to H^+ and OH^- and subtraction of OH^- from both sides of the reaction.

The change in the Gibbs free energy (ΔG) associated with any electrochemical reaction can be represented by the electrochemical potential E at equilibrium, by the fundamental relationship:

$$\Delta G = -nFE \quad (12)$$

n is the number of electrons (or equivalents) exchanged in the reaction, and F is Faraday's constant, 96,500 coulombs per mole. For Reaction 6, n is 2, i.e., the electron number change in the reaction. Electrode potential is represented by reaction 6 involving hydrogen as a reference. Thus, electrode potentials of elements that are less than that of hydrogen are negative, and those that are more than that of hydrogen are positive. The standard electrode potential of elements with hydrogen as standard (SHE) is available in tabular form in Chemical Handbooks; see Table 1 (Vanýsek 2011).

2.2 Polarization curves

The corrosion reactions, in terms of electrochemical anodic and cathodic reactions, are represented in polarization curves, also known as the Evans diagram. For the corrosion of Zn discussed above, the polarization curve is represented in Figure 3. In Figure 3(A), the anodic reaction of Zn (Equation (6)) is represented for both forward and reverse reactions with straight lines in terms of “Potential versus Current Density” in the semilog plot (Figure 3). The intersection point represents the condition when the two reactions are equal, indicating the equilibrium condition. The current density I_0 (Zn^{2+}/Zn) and electro potential E (Zn/Zn^{2+}) characterize the anodic reaction (not shown in the figure). Similarly, I_0 (H^+/H_2) and E (H^+/H_2) (not shown in the figure) represent the cathodic reaction (Equation (7)). Since the two reactions cannot be independent, the intersection of the anodic and cathodic potential curves at the

Table 1: Standard electrode potential for selected elements using hydrogen as standard (SHE).

Reaction	Standard potential, Volts ref. hydrogen
$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$	+1.438
$\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^-$	+1.358
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+1.229
$\text{Pt}^{3+} + 3\text{e}^- = \text{Pt}$	+1.2
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ (pH = 0)	+0.82
$\text{Ag}^+ + \text{e}^- = \text{Ag}$	+0.799
$\text{Hg}_2^{2+} + 2\text{e}^- = 2\text{Hg}$	+0.788
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+0.771
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ (pH = 14)	+0.401
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	+0.337
$\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$	+0.15
$2\text{H}^+ + 2\text{e}^- = \text{H}_2$	0.00
$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	−0.126
$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	−0.136
$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	−0.250
$\text{Co}^{2+} + 2\text{e}^- = \text{Co}$	−0.277
$\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$	−0.403
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	−0.440
$\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$	−0.744
$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	−0.763
$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$	−0.828
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	−1.662
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	−2.363
$\text{Na}^+ + \text{e}^- = \text{Na}$	−2.714
$\text{K}^+ + \text{e}^- = \text{K}$	−2.925

Column 1 explains the reaction involved and column 2 provides the standard potential with hydrogen as the standard. Hence it is called standard hydrogen electrode (SHE) potential.

point (I_{corr} , E_{corr}) represents the overall corrosion reaction of Zn (Equation (5)) for a given electrolyte.

Experimental curves may not be linear, but the tangential lines near the intersection are drawn, defining the intersection representing the thermodynamic equilibrium state for the corrosion of Zn. From Table 1, the electrode potential for the Zn corrosion is −0.763 V. On the other hand, the electrode potential for the reaction $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$, depicted in Figure 2, is −0.440. In essence, Zn is more electronegative, implying that it corrodes faster than Fe^{2+} , thereby protecting it. In a galvanic cell, the more negative element corrodes in preference over the less negative element, assuming the same area, as shown in Figure 3(B) (Jones 1992). Here, the standard electrode potential of M is lower than that of N. Polarization curves for a galvanic couple (GC) are shown in the figure. When the two metals are coupled, M acts as the cathode, and N acts as an anode, with the corresponding electrode potential of the galvanic couple shown as E_{corr} (GC). Note the logarithmic scale for the current density (X-axis). Concerning the sacrificial electroplated coatings,

Figure 3: (A) Polarization curves (Evans diagram) combining oxidation and reduction reactions during corrosion of zinc, defining different terms involved. (B) Galvanic couple with metal M as cathode and metal N as an anode. M corrodes protecting N, assuming the same area. From Jones (1992).

the polarization curves provide a relative corrosion protection capability under a given electrolyte environment.

2.3 Corrosion resistance and Nyquist plot

The above polarization curves provide an understanding of the equilibrium states of corrosion reactions in electrolytes. To understand or evaluate the corrosion resistance of the electroplating, Electrical Impedance Spectroscopy (EIS) study is helpful; see, for example (Garrido 2007). It is particularly relevant when the corrosion process depends on the diffusion of the reactants towards or away from the coating surface. While several articles are available online on EIS, we present only the relevant concepts needed for comparative analysis of corrosion resistance of selected electroplating conditions and materials. In short, impedance is the same as resistance as given by Ohm's law but covers AC signals. There is a phase shift in electrochemical cells, ϕ , between input voltage, E , and the observed current, I . If E_t , the potential at any time, t , is expressed as

$$E_t = E_0 \sin(\omega t) \quad (13)$$

where E_0 is the amplitude and ω is radial frequency of the signal, the output current is of the form:

$$I_t = I_0 \sin(\omega t + \phi) \quad (14)$$

The impedance, then, is the ratio between the two, similar to resistance in Ohm's law, and is denoted by:

$$Z = (E_t/I_t) = Z_0 \{\sin(\omega t)/\sin(\omega t + \phi)\} \quad (15)$$

Where Z_0 is magnitude and ϕ is the phase shift. Expressing Z using the familiar Euler's equation, we have impedance Z in terms of real and imaginary parts as:

$$Z = (E/I) = Z_0 \exp(j\phi) = Z_0 (\cos(\phi) + j \sin(\phi)) \quad (16)$$

If the real part is plotted on the x -axis and the imaginary part on the y -axis, we get the Nyquist plot relating the potential and the current. In general, since the phase shift remains the same for a given process, the magnitudes of the real and imaginary parts result in a semicircular curve (Figure 4). Axis scales are generally kept the same since they are the real (X -axis) and imaginary (Y -axis) parts of Equation (16). They are also sometimes designated as Z' and Z'' , respectively. The figures here are represented in terms of Z s or real and imaginary parts.

The Nyquist plot determined over a range of frequencies (ω) will generally take the form of one or more semicircles. The frequency decreases as one moves away from the origin. The system's response as a function of the perturbation frequency can reveal internal dynamics, such as the anodic corrosion of steel in an electrolyte. EIS is widely used as a standard characterization technique for many material systems and applications such as corrosion, plating, batteries, fuel cells, etc. If the process involves the diffusion of reactants towards or away from the surface, the resulting frequency is low. Therefore, it is represented at the right end of the Nyquist plot, as shown in Figure 4(A), for corrosion of steel in relation to the coating. In essence, the frequency dependence of this impedance in the Nyquist plot can reveal the kinetics of the corrosion reaction.

Figure 4: Nyquist plot showing the impedance of the electrochemical reaction system depicting, for example, the dynamics of the corrosion process. (A) R_s corresponds to the resistance of the solution, which can be taken as zero, and R_{ct} is electron charger transfer during the corrosion process. (B) Corrosion resistance changes with the time of exposure in the corrosive medium. The potential of the working electrode was measured against a silver-silver chloride with 3 M KCl reference electrode. The auxiliary electrode was platinum. From J. García-Antón et al. (2014).

One of the principal applications of *EIS* is in the study of electrolyte/electrode interfaces, which is widely used in the evaluation of corrosion mechanisms in metals in different environmental conditions. We believe that it is a valuable tool for the evaluation of the performance of coatings. Figure 4(B) shows the change in the impedance of Zn-coated steel immersed in NaCl solution. *EIS* measurements were performed at open circuit potential and at different immersion times in the 3.5% NaCl solution. The potential of the working electrode was measured against a silver-silver chloride with 3 M KCl reference electrode. The auxiliary electrode was platinum. With the increasing number of hours in the corrosive liquid, the corrosion resistance of the coating goes down; as can be seen from the curves. Most importantly, the *EIS* provides a tool to evaluate the coating performance in protecting the steel. It is also being explored as a tool to monitor stress corrosion cracking (Garcia-Anton et al. 2014).

2.4 Electroplating process

Several different electroplating baths have been used for plating Zn–Ni coatings. There are several review papers relating to the types of baths and the coating conditions used to obtain optimum platings, such as current density, etc. Several industry practices were developed based on their research. In addition, several additives to the bath were also experimented with to improve microstructure, appearance, and protection by the coatings. For example,

organic additives are added in small quantities (i.e., in ppm) for grain refinement, leveling, brightening, internal stress relief, and even chemical composition control (Albalat et al. 1990; Fashu and Khan 2018; Li et al. 2007; Mosavat et al. 2011; Mu et al. 2001). These additives are specific to the coatings suppliers and have been incorporated mainly through experience or trial and error approaches.

Some of the vendors further apply chromium conversion coatings after the electroplating, called passivation coatings. Trivalent chromium or tetravalent chromium protection platings are done to extend the life of the coatings and to provide enhanced corrosion protection by electroplating. Evaluation of the available conversion coatings was one of the outcomes of the US Government-sponsored initiatives in the past; see 2011 Phase II SBIR report and 2012 SBIR-STTR-US Airforce, available online, some with unlimited distribution. Some aspects of these, particularly those that involved the US Navy, will be covered in this review, as the corrosion protection under load is the predominant issue for sacrificial coatings.

2.5 Hydrogen embrittlement

The 1959 Northrop report for Armed Services Technical Information Agency identified that hydrogen embrittlement causes the delayed failure of aircraft components – see Northrop Aircraft, Inc.’s final report on ARTC Project W-95 1959. Such failures happen for the high-strength martensitic

steels used for landing gears, etc. Similar problems exist for the steels used in railroad applications. High-operating loads and corrosive service environments are on one side, and embrittling microstructures such as martensitic platelets obtained to arrive at high strengths for steels by controlled heat treatments are on the other, contribute to the delayed failures in structural steels during service.

Delayed failure occurs due to hydrogen embrittlement. In principle, hydrogen embrittlement can occur either from internal hydrogen or hydrogen from external sources, such as humid environments (Beachem 1972; Hirth 1980; Johnson 1969; Oriani 1973; Rice 1977; Tien et al. 1976); and Electroplating aggravates this problem due to the inevitable hydrogen emission during plating and further diffusion into the steel. The diffused hydrogen can get trapped inside the metal, particularly at grain and phase boundaries, microstructural heterogeneities like carbides, intermetallics, voids, etc. Atomic hydrogen in the dissolved state can become molecular at the biomaterial interfaces. When there are stress concentrations, either *in situ* generated or mechanically introduced, dissolved hydrogen diffuses towards them.

Since diffusion is a time-dependent process, the slow accumulation of hydrogen near the stress concentrations contributes to delayed failures. The external loads can be cyclic or static, but the process remains the same. The higher the strength, the higher the susceptibility of the steels to hydrogen embrittlement. Hydrogen embrittlement also occurs due to external sources, particularly when the steel components are exposed to corrosive environments. Sacrificial coatings can help to some extent if one can minimize the hydrogen ingress during the electroplating or remove it by baking, etc. Suppose the coating protection is reduced due to surface damage by impact during service or by foreign objects. In that case, the substrate metal gets exposed to corrosive environments resulting in Hydrogen Re-embrittlement. Re-embrittlement also occurs due to subsequent cleaning or brushing operations involved in maintenance applications. In essence, the stability of electroplatings and their utility in service depends on the degree of their corrosion protection and the associated hydrogen embrittlement and re-embrittlement of the substrate steel. The composition and the microstructural aspects of the steel used in service become important factors for considerations. This review covers the mechanical stability of the currently used steels, such as 4340 steel, and its modifications, such as 300M steel or AeroMet 100 steel before and after the coatings. We have reviewed some aspects of the corrosion and corrosion fatigue of 4340 steel in the past, Sadananda and Vasudevan (2015). The current

emphasis is more on the electroplating protection and related hydrogen embrittlement aspects of these high-strength alloys.

2.6 Role of residual stresses

The pre-existing internal or residual stresses will also affect the material response under externally applied stresses. The residual stresses during coatings arise from several sources (Sadananda and Holtz 2000). Mechanical incompatibilities at bimaterial interfaces involving coatings/substrates result in internal stresses that affect the integrity of the coatings and, to some extent, the substrate. The sources of internal stresses include:

- (a) Elastic modulus mismatch
- (b) Thermal coefficient of expansion mismatch
- (c) Lattice parameter mismatch
- (d) Plastic flow mismatch.

In addition to the above, compressive residual stresses are sometimes introduced in the substrate steel by shot peening before plating. Coating's process, such as plasma spray, can also introduce some stresses at the bimaterial interfaces. The resulting properties, therefore, vary depending on the specific procedures followed before and after coatings. Effects of shot peening and stresses introduced due to coating/substrate mismatches listed above are considered in accounting for specimen failures. Thouless (1991), and Evans and Hutchinson (1995) had analyzed the nature of the internal stresses generated at interfaces in coatings/substrates and the resulting material properties. In the case of Zn-Ni plating on steels, Zn has an *hcp* crystal structure, while Ni is *fcc*, and Fe is *bcc*. The actual crystal structures of both the coatings and steel depend on the compositions and the heat treatments employed. Hence, the crystallographic mismatches and the associated residual stresses can only be determined experimentally using X-ray techniques for a given case.

Residual stresses are also introduced during the backing process. The coatings are generally baked around 200 °C for 24 h to remove any dissolved hydrogen formed during the electroplating. The backing causes the thermal coefficient of expansion mismatch between coatings and the substrate, contributing to residual stresses near the coating-substrate interface. These residual stresses can be tensile, accentuating the crack initiation and growth process. On the other hand, the baking itself helps in removing hydrogen and hence remains beneficial for the coated steel.

2.7 Hydrogen embrittlement evaluation tests

Delayed failures due to hydrogen embrittlement are evaluated using slow strain rate tests that help determine the threshold stress-intensity factor during stress-corrosion tests, using the sharp-notched or the fracture-mechanics type of specimens. The diffusion of hydrogen and its segregation near the stress concentration depend on the diffusion rates in a given material. They vary with the microstructure of the steel and the test temperature. The delayed times for failure due to diffusion of hydrogen are generally evaluated as a function of stress. Delayed failures also occur under cyclic loads. We have shown that fatigue damage involves two load parameters, maximum stress ($\sigma_{\max}$) and amplitude ($\Delta\sigma$). For crack growth, these two parameters correspond to the maximum stress intensity factor ($K_{\max}$) and amplitude (ΔK). The time-dependent effects enter via the $\sigma_{\max}$ or $K_{\max}$. The fatigue data for hydrogen embrittlement requires proper analysis for evaluation. Since time is a factor, the number of cycles for failure also depends on frequency and hold-time at the peak loads. The R -ratio effects also get affected since, at high R -ratios, the magnitudes of $\sigma_{\max}$ or $K_{\max}$ are high. Unfortunately, most of the tests using electroplated materials have been limited to one or two R -ratios, and therefore do not fully depict the material response in service. They, however, help in comparing the performance of a given coating with others. This review examines the two-parametric nature of fatigue damage in terms of hydrogen embrittlement during cyclic loads of both substrate and the coatings to the extent possible. The time-dependent aspects of the failure process will be examined for steels with and without coatings.

2.8 Diffusion of hydrogen in steels

Hydrogen embrittlement occurs by diffusion of hydrogen to the stress concentration. It means that the delayed failure is intimately connected with the diffusion kinetics on one side and the embrittlement mechanism on the other. For sacrificial coatings, diffusion kinetics via the coating materials also becomes important. It is in addition to the hydrogen traps and binding energies of the hydrogen with the traps. Figure 5 shows the diffusion rates in steels with ferritic or austenitic microstructures as a function of $1/T$, where T is the test temperature. The data were collected from Badeshia (2016).

Figure 5: Diffusion rates in ferrites and austenites in relation to Ni, Cd, Sn, and some oxides and carbides. From Badeshia (2016).

The figure shows that diffusion rates are very high in ferrite. Next is ferrite with hydrogen traps. As mentioned before, the hydrogen traps could be grain or phase boundaries, carbides, intermetallics, etc. The diffusion rate in nickel is also shown as it is related to the Zn–Ni coatings. The diffusion rates in austenite are comparatively lower, supporting that austenitic stainless are less susceptible to hydrogen embrittlement. The figure shows that the diffusion rates in Cd are much lower than that of nickel, indicating why it was more suitable for coating but for its toxicity. Other hard coatings such as Al_2O_3 are also used to protect the steel, but they do not act as sacrificial coatings. In essence, the kinetics of hydrogen diffusion play a prominent role in the stability of the coatings and the substrate steel.

The above background provides various aspects involved in understanding the sacrificial electroplating of high-strength steels. Several other variables are important such as electroplating solutions, pH, current density used, additives to the bath, stirring speeds, the backing after the plating, and the condition of the substrate before and after plating, etc. Some specifics are related to the coatings process used by suppliers or researchers. As mentioned before, chromium conversion coatings are also employed in service to protect the coatings and substrate. The effects of these on the life of the structural steels will be discussed as needed.

2.9 Hydrogen traps and trap-binding energies

Hydrogen emission and subsequent diffusion into the metal get aggravated by the presence of hydrogen traps. These include the vacancies, voids, grain or phase

boundaries, substitutional elements into the steel, their carbides and sulfides formed during subsequent processing, and dislocations present in the plastic zones. Unfortunately, the hydrogen binding energies at these traps are low enough that hydrogen gets released under applied stresses at ambient conditions contributing to further embrittlement, causing delayed failures. Table 2, taken from Badeshia (2016), gives the binding energies of some of the traps typically encountered in steels. Here, α stands for ferrite, and γ stands for austenite phases. These binding energy values were collected from various sources, as stated by Badeshia. Most of the binding energies are sufficiently low. Hence, trapped hydrogen can get released from these and diffuse towards stress concentration regions, causing delayed failures. The consensus is that binding energy higher than 100 kJ/mol is safer since releasing hydrogen from such a trap is difficult at ambient temperatures and will not contribute to the delayed embrittlement.

The above broad background is provided since understanding the performance of electroplated high-strength steels requires a multidiscipline approach, as stated before.

Table 2: Hydrogen binding energies at different trap sites in steels.

Trap site	Trap energy –Eb (kJ/mole)
Single iron-vacancy	49–78
Single iron vacancy (different estimation)	24–29
Cr, Mo, and V atom	26–27
Mn atom	11
Ni atom	–12
C atom	3
Al atom (in γ)	6
Ti atom	26
General grain boundaries	32
γ/α interface	52
Dislocation stain field	23–27
Dislocation core/jogs	60
Microvoids	48
ϵ -carbide	65
Cementite/ α interface	11–18
TiC	46–116
$\text{Fe}_{1.2}\text{Ti}_{0.8}\text{S}_2$	58
V_4C_3	33–35
Coherent M2C (Mo-rich needles)	11–12
MnS	72
MnS/ α interface	72
Iron oxide/ α interface	51–70
$\text{Y}_2\text{O}_3/\alpha$ interface	70
$\text{Al}_2\text{O}_3/\alpha$ interface	79
N atom	13

Hydrogen gets released from traps that have low binding energies (from Badeshia 2016).

3 Performance of high-strength steels with or without sacrificial coatings

3.1 Performance of high-strength steels

Because of its importance, extensive work has been done on the hydrogen embrittlement of high-strength steels, Figure 6. The failure time under a sustained load decreases with increasing applied stress. Here, hydrogen was introduced by cathodic charging. Steel with higher strength is more susceptible to embrittlement (Slaughter et al. 1955). Johnson et al. (1958) also evaluated the electroplated, hydrogenated, baked, and notched tensile specimens under sustained loads. They showed that the failure time decreases with an increase in stress and hydrogen concentration, Figure 7. The results indicate that even at low concentrations (45 ppm) of hydrogen, the delayed failure occurs for the high-strength steels used in structural applications. The early work by Brown and Beachem (1965) of NRL shows that fracture toughness and the threshold stress intensity for stress corrosion crack growth decreases with an increasing yield stress of 4340 steel, Figure 8.

Later, Townsend (1975), showed that the incubation time for crack initiation in 4140 steel after coating decreases with increasing strength, as measured by Rockwell hardness. It is significantly lower than that of uncoated (bare) steel with the same hardness (Figure 9). In principle, baking helps to remove hydrogen introduced during plating.

Figure 6: Failure time under sustained load for 4340 steel after cathodic charging increasing the ultimate tensile strength (UTS) of the two steels reduces the failure time. From Slaughter et al. (1955).

Figure 7: (A) Incubation or delayed time for crack initiation in hydrogenated, plated, and baked 4340 steel as a function of applied stress. (B) Failure time for notched specimens as a function of applied stress and hydrogen concentration. From Johnson et al. (1958).

Figure 8: Brown and Beachem's early work at NRL (1965), showing the threshold for stress corrosion crack growth and fracture toughness decrease with an increase in the strength of the 4340 steel.

Figure 9: The crack initiation time decreases with increasing strength (hardness), and more so for Zn-coated steel compared to uncoated (bare) steel. From Townsend (1975).

Baking temperature and times are important. Temperatures cannot be too high to affect the microstructure of the substrate steel. Figure 10, from Fontana and Green (1978), shows the effect of baking time at temperature 150 °C after the steel is hydrogen charged. The data indicate that at least 24 h of baking at 150 °C is required to regain the original strength.

Gangloff (2003) has shown that the threshold stress intensity of crack growth, K_{th} , under sustained load decreases with an increase in hydrogen pressure and level off at high pressures, Figure 11. At low pressures, the limiting value should correspond to the fracture toughness, K_{IC} . Leveling off with increasing hydrogen pressure implies

that the environment alone cannot independently contribute to crack growth. Some minimum stress is essential for crack initiation and growth. In essence, the hydrogen reduces the stress needed for crack growth and failure. Component failures, therefore, occur predominately under stresses but are assisted by a crack tip environment.

There have been several efforts to evaluate the life under sustained load and fatigue of steels used in structural applications. Speidel (1982) has done a lot of work on stress corrosion crack growth and fatigue in various environments. The fatigue life of high-strength steels is affected even in

Figure 10: Effect of baking at 150 °C to remove hydrogen after charging on sustained load failure in high strength 4340 steel. Baking helps to remove dissolved hydrogen. From Fontana and Green (1978).

Figure 11: Effect of hydrogen pressure on the threshold stress intensity factor for crack growth under sustained load for high strength steels at room temperature. From Gangloff (1986).

ambient air due to humidity which contributes to environmentally induced hydrogen embrittlement. Figure 12 shows the endurance limit (10^7 cycles) of low carbon steels in normalized and tempered (martensitic) conditions as a function of UTS in ambient air, aerated, and saltwater environments. Speidel has determined fatigue crack growth rates in high strength 4340 steel in distilled water environment as a function of frequency (Figure 13). He has plotted the crack growth rates, da/dN , as a function of stress intensity factor range, ΔK , for various frequencies tested and compared the results with data in a vacuum of 10^{-5} Torr (Figure 13(A)). With decreasing frequency, the crack growth rates initially increase sharply but later level off until they join the same

line, perhaps indicative of pure fatigue behavior. The increase is larger with decreasing frequency. Since the environmental effects are predominately time-dependent, we have replotted the data in terms of da/dt versus K_{max} in Figure 13(B).

Interestingly, the figure shows how the material response slowly changes from cycle-dependent to time-dependent crack growth behavior. The vacuum data are also shown for comparison. The crack growth rates at 4 Hz initially are close to the vacuum data but increase rapidly and seem to level off, characteristic of State II crack growth under SCC. As the frequency is decreased from 1 to 0.1 Hz, the da/dt data moves slowly towards the right, merging with the data corresponding to still lower frequencies, 0.01 and 0.001 Hz. At the low frequencies, the apparent Stage II behavior of SCC is seen. Thus, the crack growth behavior moves from cycle-dependent behavior to time-dependent behavior with crack growth rates governed by the K_{max} than ΔK .

Figure 13 demonstrates that the time and K_{max} dependent corrosion process gets superimposed on fatigue, even in ambient air, resulting in superimposed corrosion-fatigue crack growth. These superimposed K_{max} dependent processes can be quantified easily using the crack growth trajectories under cyclic loads arrived at by using our two-parametric approach developed in the past, see, for example, Sadananda et al. (2003). Figure 14 shows the fatigue crack growth data in high strength 300M steel (a modified version of 4340 steel) by Ritchie (1977). Historically, the load ratio effects (R -effects) have been attributed to crack closure. We have shown that most of the R -ratio effects arise due to two parameters ΔK and K_{max} , controlling the fatigue crack growth, Sadananda et al. (2003). If

Figure 12: Fatigue endurance limit of low carbon steel in normalized and tempered condition as a function of UTS in corrosive environments, after Speidel (1982).

Figure 13: Fatigue crack growth of high strength 4340 steel in distilled water as a function of frequency. Vacuum data at 10⁻⁵ Torr is shown for comparison. (A) Crack growth rates as a function of amplitude, ΔK . (B) Crack growth rates, da/dt , represented in terms of K_{max} , after Speidel (1982).

any superimposed K_{max} dependent process is present over and above the fatigue, then the resulting crack growth trajectories deviate from the pure fatigue line. The extent of deviation varies with frequency if the process is time-dependent.

Figure 14 shows the crack growth rates deviate from the pure fatigue line, and the deviation is larger for the higher stress steel. The points AA in the trajectory correspond to the same crack growth rates in the two steels. The horizontal shift from the pure fatigue line, in principle, corresponds to the excess K_{max} component involved in the excess crack

growth contribution from the time-dependent process. With decreasing test frequencies, the shift from the pure fatigue line will be larger. At very high frequencies, the crack growth becomes purely cycle-dependent, merging with the ΔK - K_{max} line. Suppose the crack growth rates become a completely time-dependent process. In that case, the trajectory runs parallel to the X-axis, or it plunges towards the K_{max} axis if the K_{max} parameter fully controls it. In that case, ΔK will not have any role. Such behaviors have been observed in the past, particularly for materials tested in very corrosive environments. For example, the crack growth

Figure 14: (A) Effect of yield stress on the fatigue crack growth rates in 300 M steel tested in ambient air. (B) Crack growth trajectory arrived at using the two-parametric approach. Crack growth trajectory deviates from the pure fatigue line indicating a superimposed K_{max} dependent process. The deviation is more for higher-strength steel. Each data point in the trajectory represents a crack growth rate in Figure B. AA in Figure B corresponds to the same crack growth rates in the two steels. Data from Ritchie (1977). Trajectory analysis from Sadananda et al. (2003).

trajectory for 4340 steel at low frequencies (see Figure 13) could plunge into the $K_{\max}$ -axis; the required R-ratio data, however, is not available to show that behavior.

The hydrogen that gets observed by traps (Table 2) can get released under applied load, diffusing towards the crack tip, contributing to hydrogen embrittlement and thus lowering the crack growth threshold. McMahon et al. 1980, did an extensive analysis of the effects of manganese and metalloid additions to the steel on stress corrosion crack growth. Figure 15 shows the threshold stress intensity decreases with the increase in the concentration of these elements, which either directly contribute to embrittlement or aid in the process by acting as hydrogen traps, Bandhopadhyay et al. (1983). Figure 15(B), taken from Tvrdy (1977), shows that the threshold-dependence on the yield Stress increases as the test environment changes from the ambient air to NaCl to the hydrogen environment, indicating the hydrogen contributes to considerable degradation of the steel. In all cases, the threshold levels off to saturation level with increasing concentration of the damaging species. The saturation threshold varies with the environment and is most severe with hydrogen. We note that the hydrogen diffusion controls the embrittlement kinetics, as demonstrated way back by Oriani and Josephic (1974), see Figure 16. Interestingly, the slope is close to 0.5, indicating that the threshold varies with the square root of H concentration, expected for a diffusion-controlled process. Understandably, being a heavier atom, the threshold stress is higher for deuterium than hydrogen.

3.2 Evaluation of Zn-Ni coatings

Significant efforts are being made to replace the Cd coatings with Zn-Ni or its modifications using the electroplating process. Most of these efforts are being made under government-sponsored projects and research efforts by the universities under sponsorship. In the following, we present the available data in the open literature regarding the performance of these coatings compared to that of Cd coatings. The effects of the coating-process variables that affect their performance will also be noted. Since hydrogen

Figure 16: Crack growth is diffusion-controlled – higher stresses are needed for deuterium due to its heaviness.

Figure 15: (A) Example showing threshold, K_{th} , approaches a limiting value as a function of concentration, indicating that the chemical effects get saturated. (B) Examples showing the threshold K_{th} levels of a limiting value as a function of yield stress. From (A) Bandhopadhyay et al. (1983), and (B) Tvrdy (1977).

emission and its pick-up by the coatings and the substrate steel are inevitable during electroplating, the role of hydrogen embrittlement with or without coatings is an important consideration for the stability of the coating and the substrate. The recent concentrated efforts in developing compositionally modulated multilayer coatings of Zn–Ni will also be examined. Their performance will be compared with that of monolithic coatings. Some efforts are also being made to add a third element that can enhance the performance of the Zn–Ni coatings.

3.2.1 Examination of Zn–Ni phases formed during coatings

It is important to examine the phases that form during plating in relation to the equilibrium phase diagram available in the literature. Figure 17(A) is the standard Zn–Ni phase diagram, ASM Handbook (2016). Based on several reports, it appears the Zn–Ni coatings with Ni concentration around 14 wt. % is ideal for protection by the plating, as indicated in Figure 17(A) by the arrow-line. Based on the plating solutions and the phase diagram, Zn is expected to deposit first. Experimental results, however, indicate that a thin layer of Ni deposits first. Afterward, a substitutional solid solution of Ni in Zn gets deposited. The first deposited thin layer of Ni formation is considered anomalous since no rational explanation could be given. With increasing Ni content, based on the X-ray analysis, Sriraman (2012), in his thesis, establishes that the actual phases present as a function of Ni wt % and are indicated in Figure 17(B).

Experience with the coating process indicated that alkaline plating baths are preferred instead of acid baths in industrial applications. It appears that the thickness of the

coatings is more uniform with alkaline plating solutions. In addition, the resulting microstructures are also found to be more uniform. The alkaline baths provided uniform columnar platelet-microstructure, which seems to be preferred over the lamellar microstructure from the acid-baths (Winand 2010).

Considering Zn is *hcp*, the addition of Ni (*fcc*) in Zn-matrix decreases the ‘c’ axis while increasing the a-axis when the substitutional solid solution is formed. The coating is on steel which is essentially a *bcc*, Fe (α). Residual stresses are introduced during this atomic mismatch. The solid solution of Ni in Zn extends up to 7.4% Ni. Beyond that, a non-stoichiometric intermetallic δ -phase forms. Above 11% of Ni, there is a two-phase region with δ and γ phases. Beyond 13% of Ni, it becomes entirely γ -phase. In this region, Ni > 13%, the plating results in fine grain structure with the even distribution of platelets and reduced surface roughness. It also covers the substrate surface evenly. The residual stresses due to plating get stabilized at these compositions. Hence, experience indicates that the performance of the Zn–Ni coatings seems to be the best when the plating has γ -phase, with 14% Ni.

There is no clear consensus on the structure of the γ -phase. From the phase diagram, the γ -phase field extends up to 24% of Ni. Some consider it as intermetallic with $\text{Ni}_2\text{Zn}_{15}$ with defects, while some describe it as a sublattice structure with no particular stoichiometry ascribed to it. Heike et al. 1936, describe its structure that correlated with the formula NiZn_3 corresponding to the composition where the congruent melting of this phase takes place. Another report says its stoichiometry corresponds to $\text{Ni}_4\text{Zn}_{22}$ (Johnsson et al. 1968). From our point, it is sufficient to

Figure 17: (A) Zn–Ni phase diagram, ASM Handbook. (B) Actual phases present in the coatings. From Sriraman (2012).

understand that it has some range of compositions, and the ideal for plating seems to correspond to close to 14 wt. % Ni.

Besides, the microstructure of the coating depends on the coating variables in addition to acidic versus alkaline bath. These variables include a) the types of additives used, b) stirring speed, and c) current density. Some of the coating conditions are industry-specific. Only those available in the open literature are based on government-funded efforts for research analysis. These are discussed here with proper credit to the source. For example, optimum pH, stirring speed, and current density are required to get dense, uniform coatings with fewer interfacial defects. These interfacial defects can act as hydrogen traps. Conde et al. (2011) have shown that the microstructure changes with the changing plating conditions in terms of current density and/or stirring speed. The formation of the first layer of Ni is mostly beneficial since the hydrogen diffusion rates are relatively low in Ni (see Figure 5). However, for the same reason, the Ni-layer makes it difficult for already trapped hydrogen to escape.

3.2.2 Effects of coating on the properties of the substrate

Several properties have been evaluated after electroplating and compared with those of the base materials. Some of the properties include the adhesion of the coating, protection against corrosion, nature of the polarization curves, Nyquist plots with and with coatings, slow strain rate tests, fatigue life with or without notches, and with or without prior shot peening of the substrate, etc. For some of the above tests, the reported results are in the form of pass/fail

criteria or the number of hours it took for the appearance of red rust on the surface, etc. We present here only the data that are quantifiable and comparable in terms of other coatings in the literature. For other information, specific referenced reports need to be examined. We restrict our discussion to the high-strength materials used in the service, such as 4340 steel or its modified alloy 300M steel, AeroMeet 100 steel, etc., which are currently used in aircraft and railroad industries.

The Navy-supported program evaluated the Zn-Ni coatings from two industrial sources, with two types of conversion coatings on the electroplating. These results were compared with that of Cd electroplating, Figure 18. The coatings were done on both shot-peened and not-shot-peened specimens to evaluate the benefits of the compressive stresses introduced during shot-peening. Conversion coatings are used in the industry on top of the electroplating to enhance the performance of the coatings during the service of the steel. The fatigue tests were done predominately at $R = -0.3$, while some tests were done at $R = -0.5$. The results indicate that in the un-peened condition, the fatigue life of Zn-Ni coated steel is slightly lower than uncoated steel. The results, however, seem to merge for 10^6 cycles and above. In the above figure, two Zn-Ni coatings identified as 'Dip and Ato' with two conversion coatings Hex (hexavalent) and Tri (trivalent) have been used. Dip stands 'Dipsol™ IZ-C17+ LHE Zn-Ni' plating and Tri stands for IZ-264 Tri corresponds to trivalent chromium conversion coatings. LHE stands for low hydrogen embrittlement, i.e., the coated specimens were baked after electroplating to remove any hydrogen diffused into the metal during electroplating, see Figure 10. Likewise,

Figure 18: Fatigue of electroplated 300M steel with Zn-Ni and Cd coatings, followed by chrome conversion coating. Two commercial sources of platings, and two conversion coatings were evaluated under the Navy-supported program. Coatings were evaluated for both (A) peened and (B) not-peened specimens, in ambient air, cycled at 5 Hz.

Ato stands for 'Atotech™ ZNA Zn-Ni plating,' and Hex stands for hexavalent chromium conversion coating. Various steps involved in coatings are given in the funded reports; some are available online with a wider distribution.

Comparison of Figures 18(A) and (B) indicate that for a given applied stress, the shot peening enhanced life slightly. Figure 19(A) further compares the effect of coating of peened and not-peened coated versus bare on fatigue lives of Zn-Ni coatings of 300M steel, and Figure 19(B) compares the fatigue lives of Zn-Ni coatings versus Cd coatings. The fatigue lives with Zn-Ni coatings seem to be slightly lower compared to those with Cd. The results, however, are not statistically significant due to the limited number of tests. The differences in lives are also small. Further evaluation of the Zn-Ni coatings compared with that of Cd coatings was done to evaluate resistance to hydrogen embrittlement using notched specimens. While both coatings passed a 200 h sustained load test at stresses correspond to 75% of notch fatigue strength (NFS), careful analysis of the cross-sections at the notched area revealed that Zn-Ni coating thickness was more uniform compared to that of Cd coatings.

Figure 20 shows the fatigue lives of both Zn-Ni and Cd coated and uncoated 4340 steel. The results seem to be different from those of 300M and AeroMet 100 Steels (Figure 19). Note that the scales in the two figures are also different. On the other hand, the microstructure of 4340 steel could be more susceptible to hydrogen embrittlement. It is perhaps one reason why 300M steel, a modified version of the 4340 steel, was developed to overcome this HE problem. In both cases, the number of specimens tested was again limited, particularly for the fatigue-life characterization,

under this program. The results, however, provide some guidelines in terms of the efficacy of Zn-Ni coating in contrast to that of Cd coatings.

Figure 21(A) presents data from Bel Air, perhaps under a different Govt. sponsored program, showing that the fatigue lives of 4340 steel with both Zn-Ni coatings and Cd Coatings do not differ from those of uncoated steel. In Figure 21(B), data generated by Eun Lee et al. of NAVAIR (2013) on the same steel are shown, but with Cd coatings. The results indicate that the fatigue lives of bare and coated 4340 steel do not differ significantly in the ambient air. They have also evaluated the performance of the coatings in a 3% NaCl environment and show a) that the fatigue lives are lower in the corrosive environment and b) the coated materials performed better than uncoated

Figure 20: Electroplating, however, appears to decrease the fatigue life of 4340 steel for both Zn-Ni and Cd coatings, indicating that the microstructure of 4340 steel is more susceptible for HE.

Figure 19: Additional data from Navy SBIR. (A) Comparison of fatigue lives of peened and not-peened and Zn-Ni coated and bare 300M steel. (B) Comparison of fatigue lives of Zn-Ni coated versus Cd coated AerMet 100 steel with not-peened specimens.

Figure 21: (A) Additional data on 4340 steel from Bell-Helicopter under a different SBIR program showing the data for both coated and uncoated falling on the same S-N curve. (B) Eun Lee data on Cd coatings of 4340 steel under three different coating conditions.

material. Figure 22 presents a more recent independent study of fatigue life of 4340 steel in 3.5% NaCl water using both Zn-Ni and Cd coatings on smooth and surface-dented (SD) specimens, Alzahrany (2017). The study was done at two different R-ratios, Figure 22(A), and two different frequencies using the two types of specimens, at $R = 0.1$. The results indicate that at $R = 0.3$, within the scatter, both fatigue lives are nearly the same. With the fatigue at $R = 0.1$, the lives are lower than those at $R = 0.3$. The surface dented specimens were tested only at $R = 0.1$. The results again show that they are not much different from those of the

smooth specimens. Figure 22(B) shows that there is more spread in the data as a function of frequency.

Nevertheless, it is difficult to conclude that one coating is better than the other or there is a notable frequency effect in the range of frequencies tested. Unfortunately, the number of tests done under fatigue is limited and prevents us from arriving at any significant conclusion based on the data. However, it provides some assertion that Zn-Ni coatings are as good as Cd coatings in NaCl environment. Figure 23 presents even more recent test data on 4340 steel with Zn-Ni and Cd coatings, Fernandes et al. 2020. The

Figure 22: A more recent study of fatigue life in saltwater of both Zn-Ni and Cd coated 4340 steels. (A) Data at two R-ratios and with smooth and surface dented (SD) specimens. (B) Effect of frequency on fatigue life for both Zn-Ni and Cd coated 4340 steel using smooth and SD specimens. From Alzahrany et al. (2017).

results of Zn–Ni coating were slightly better than those of Cd coatings. The authors report that the average thickness of Zn–Ni coatings was around $(3.00 \pm 1.0) \mu\text{m}$ while that of Cd coatings was $(11.3 \pm 2.0) \mu\text{m}$. The residual stresses near the coating-substrate interface can vary with the thickness of the coatings.

3.3 Role of residual stresses

Shot peening is normally done to specimens before electroplating. Thus, the compressive residual stresses introduced by shot peening can be considered as preexisting. The coating introduces additional residual stresses in terms of an elastic mismatch between the coatings and the substrate. If coating involves other processes, such as plasma spray, the process itself can introduce residual stresses in the coatings. Voorwald et al. 2005 have shown that residual stresses introduced during coating depend on the thickness of the coatings. They can affect the fatigue life of the coated specimens, as shown in Figure 24. The compressive stresses are higher in the base metal due to shot-peening. With the initial coatings, these stresses are significantly reduced. It could be due to tensile stresses introduced due to lattice parameter mismatch at the coating/metal interface. However, as the thickness of the coating increases to 15–21 μm , these coating-introduced tensile stresses get slowly eliminated, leaving the original compressive residual stresses introduced by shot-peening. Figure 24(B) shows the corresponding fatigue life of

coatings with various thicknesses. In this figure, the authors also compared the life of coatings with Cd and Cr coatings, each with a different thickness. The fatigue life is affected by the residual stresses and hydrogen embrittlement introduced during the plating process, as discussed before.

3.4 Resistance to corrosion

3.4.1 Polarization curves

Corrosion resistance has been evaluated using polarization curves (Figure 3), and Nyquist plots developed using electrical impedance spectroscopy (ESI) (Figure 4). While the polarization curves provide the thermodynamic state, the ESI provides dynamic aspects of the corrosion resistance of the coating/substrate in each electrolyte. It is also possible to follow the progressive corrosive behavior using the ESI, which measures the resistance (impedance) of the coating/substrate system.

The polarization and Nyquist plots provided here are intended only for relative comparison purposes. For actual test conditions and standards used in generating these plots, which may differ from one investigator to another, the reader is referred to the original papers for details. The test parameters from the referenced authors are provided to the extent available. Unless otherwise specified, standard electrode potential for selected elements using hydrogen as standard (SHE) is assumed.

Corrosion at specific locations can be followed for a given corrosive electrolyte. In addition, the time-dependent corrosion behavior can be examined using EIS. Figure 25, for example, shows the effect of Ni addition to Zn on both the polarization curves and the corrosion resistance curves (Nyquist plots), Tafreshi et al. (2016). Based on their micrographs, one can estimate the thickness of their coatings is around 0.8 mm. They have used a ‘three-electrode cell with a platinum foil (1 cm^2) as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. The tests were performed at room temperature in 3.5 wt. % NaCl solutions. The scan rate was 1 mV/s during the polarization tests. The EIS measurements were made at open circuit potential with superimposed 5 mV sinusoidal signal amplitude in a frequency range of 100 kHz to 0.01 Hz. They considered the standard potential of Zn, Ni, and St37 steel as -760 , -250 , and -440 mV, respectively, in their discussion in accounting for the relative corrosion (see Table 1). Figure 25(A) shows the polarization curves of electroplating of Zn and Zn–Ni coatings with different wt. % of Ni to evaluate the best coatings for corrosion protection. Corrosion potential (E_{corr})

Figure 23: Another independent study of Zn–Ni and Cd coated 4340 steel in ambient air showing Zn–Ni is as good if not better than Cd coatings for 4340 steel. The life of the threaded specimen is lower than that of the smooth specimen due to pre-existing stress concentrations.

Figure 24: (A) Residual stresses depend on the thickness of the coatings affecting (B) the fatigue properties. From Voorwald et al. (2005).

Figure 25: Change in the corrosion potential and resistance to corrosion by the addition of Ni to Zn in the electroplating. Measurements were made using electrode cell with a platinum foil (1 cm^2) as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. (A) The polarization curves with an increasing percentage of Ni content in the coatings. (B) changes in the corrosion resistance with Ni addition as revealed by Nyquist plots. From Tafreshis et al. (2016).

and corrosion current (i_{corr}) were extracted using the Tafel extrapolation methods, and the results are presented in Table 3.

Figure 25(A) shows that the corrosion potentials of the Zn–Ni alloy coatings are nobler than Zn coatings (i.e., more

Table 3: Effect of wt. % Ni in Zn–Ni coatings on the corrosion potential (E_{corr}), corrosion current density (i_{corr}).

Plating type	i_{corr} ($\mu A/cm^2$)	E_{corr} (mV)
Zn	11.0	–1238
Zn-11 wt. %Ni	6.4	–823
Zn-14%Ni	1.0	–643
Zn-17%Ni	8.6	–987

These values are extracted from the polarization data of pure Zn and Zn–Ni Coatings presented in Figure 25.

positive). The results also show that Zn–Ni alloy coatings have lower corrosion current densities than Zn coatings, indicating their higher corrosion resistance. In addition, the results indicate that in comparison to 11 wt. %Ni or 17 wt. %Ni, Zn with wt. %14 Ni has high corrosion resistance. From the phase diagram, Figure 17(A), the 14 wt. % Ni seems to be ideal for the coatings with γ -phase formation. Based on the phase diagram, higher or lower wt. %Ni can result in dual phases, perhaps contributing to local galvanic corrosion in the presence of a corrosive medium. Increased corrosion rate, early crack formation in the coatings due to residual stresses, and hydrogen evolution could also be a problem in the dual-phase Zn–Ni coatings. Other researchers have also reported similar results.

Figure 25(B) shows electrochemical impedance spectroscopy in terms of Nyquist plots and the effect of Ni addition to the Zn plating. Usually, the Nyquist plot will be a semicircle, as in the case of Zn in the figure. The semicircle for Zn represents the resistance of the coating and the electrolyte, see Figure 4. For Zn–Ni coatings, the curve gets modified from semicircle as one moves to lower frequencies (away from the origin). The authors attribute this to the formation of protective corrosion products on the coatings, which become more evident in the Bode plots (not shown here). In simple terms, an increased radius or the size of the Nyquist plot indicates increased resistance to corrosion by the protective film. Figure 25(B) indicates that Zn with 14 wt. % Ni has the highest corrosion resistance compared to Zn with 11 of 17 wt. % Ni. It further confirms that Zn with 14 wt. % Ni is ideal for corrosion protection of the substrate steel.

Extensive analysis of corrosion resistance and the tribological aspects of the electroplated Zn–Ni coatings compared with those of electroplated Cd coatings have been done by Sriraman (2012) as part of his Ph.D. thesis at McGill University (See also Sriram et al. 2012, 2013). Some essential aspects pertinent to our analysis are presented here. The Zn–Ni electroplatings were obtained from two commercial sources that use their standardized procedures, similar to what was reported before under Navy-supported programs. The Zn and Cd electroplatings were made using industrial plating facilities. Sriraman (2012) also studied the performance of Cd–Ti coatings on steel. Zn–Ni coatings on steel tested were from:

- Boeing low hydrogen embrittling process of Boeing Co. For simplicity, these coatings will be referred to as *BZn–Ni* coatings.
- Dipsol Iz C17+Zn–Ni commercially available coatings. These will be referred to as *D–Zn–Ni* coatings.
- Zn-electroplatings were done using commercial additives. These were done at a laboratory-scale set-up.
- LHE Cd plating was obtained in an industrial facility using an alkaline-based plating solution. It will be referred to as Cd or LHE Cd coatings.

The thickness of all coatings was maintained in the range of 15–20 μm . The coatings contain δ to γ phase with an average of 10–14 wt. % Ni, based on the X-ray analysis.

Some tests were done with or without the post-baking treatment after plating and some with or without the trivalent Cr conversion coatings. Conversion coated specimens will be referred to also as passivated coatings. The passivation involves a formation of a layer of trivalent Cr oxide of ~50 nm thick that helps to prolong the life of the coatings. Thus, Zn–Ni coatings were tested under four

conditions: 1) as-plated, 2) with chromate passivation, 3) as plated and baked, and 4) plated, passivated, and baked. The baking is done at 200 °C for 24 h, a commercially adopted practice to remove hydrogen dissolved during platings; see example in Figure 10.

The author provided the following details for his measurements. ‘The open-circuit potentials (OCP) of the coatings were measured using a potentiostat in a three-electrode electrochemical cell, where the coating of interest acts as a working electrode, a platinum wire as a counter electrode, and a standard saturated calomel electrode as a reference. The OCPs were monitored for 24 h, and subsequently, the electrodes were polarized potentiodynamically in a continuous sweep. The rate of the potential sweep was 1.66 mV/s and the scanning potential range varied from –250 to 250 mV with respect to the OCP. The E_{corr} and I_{corr} were determined from the intercepts by Tafel’s extrapolation method. EIS was also performed in a three-electrode electrochemical cell, as mentioned above in a computer-controlled potentiostat. The EIS spectra for the coatings were acquired at OCP with AC frequencies ranging from 105 Hz to 10^{–3} Hz and an amplitude of 10 mV. The impedance spectrum was acquired at a time interval of every 4 h resulting in data acquisition at the end of 4, 8, 12, 16, 20, and 24 h. For all the electrochemical characterization, the medium used was 3.5% NaCl solution which simulates the marine environment.’

The potentiodynamic polarization curves for the coatings are given in Figure 26. They are as-plated, and as-plated and passivated by trichromium conversion coating conditions for Boeing (*B*) and Dipsol (*D*) coatings. Both coatings showed similar polarization potentials, and they are sufficiently negative, Figure 26(A), indicating that both will sacrificially protect the substrate steel. That is, they corrode before the steel corrodes. The figure also shows that baking has not affected the potentiodynamic response of the coatings. Figure 26(B) shows the curves for the same coatings but after Cr passivation or conversion coatings. The effect of baking on the polarization curves is also shown. For *D*-coatings, passivation increased the potential a little bit but not much. The corrosion protection is slightly enhanced by passivation. However, for *B*-coatings, the effect of passivation is more pronounced. In the plated and passivated condition, the electrode potential seems to have decreased (compare Figure 26(A) and (B)). However, baking after the passivation seems to have improved coatings’ resistance to corrosion.

The electrode potentials for *B* and *D* coatings are nearly the same, Figure 26(B). Table 4 below provides the E_{corr} , and I_{corr} values arrived at by Tafel’s extrapolation method. The author mentions that the I_{corr} is higher after baking,

Figure 26: Polarization curves for Zn-Ni electroplate coatings. (A) with or without baking after plating, (B) with or without baking after plating and passivating by a conversion coating. The thickness of all coatings was in the range of 15–20 μm . The potentials were measured using a three-electrode electrochemical cell platinum as a counter electrode and a standard saturated calomel electrode, SCE, as a reference. From Sriraman (2012).

and generally, the values are higher for *B*- than *D*-platings. Possibly it reflects the rate of dezincification and distribution of corrosion products on the coating surface. The X-ray analysis of the coating surfaces indicated that dezincification does occur changing γ -Zn-Ni to δ -Zn-Ni (see phase diagram Figure 17). Based on the X-ray data, the primary corrosion product appears to be close to $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, which provides additional protection to the Zn-Ni coated steel. The analysis supports that Zn-Ni coatings provide as good, if not better, protection than Cd coatings.

Electrochemical impedance spectroscopy study was also made on all the coatings as it can help identify the corrosion process and the kinetics, which polarization plots cannot give. In analogy with the circuit theory, Nyquist plots depict the change in the resistance that can be related to the resistance to corrosion. Usually, a semi-circle gets distorted with changing resistance with time.

Table 4: Corrosion current and electrode potentials of Zn-Ni coatings with or without subsequent treatments (from Sriraman 2012).

Coating	Treatment	Corrosion potential E_{corr} (V)	Corrosion current i_{corr} (A)
B-Zn-Ni	As applied	-0.78	0.627
D-Zn-Ni	As applied	-0.77	0.997
B-Zn-Ni	As applied & baked	-0.78	0.554
D-Zn-Ni	As applied & baked	-0.77	0.512
B-Zn-Ni	Passivated	-0.89	1.638
D-Zn-Ni	Passivated	-0.77	0.768
B-Zn-Ni	Passivated & baked	-0.72	1.9
D-Zn-Ni	Passivated & baked	-0.72	2.096

Figure 27 compares the corrosion resistance of Zn-Ni coatings with those of Cd and Cd-Ti coatings. Figure 27(A) shows that *D*-Zn-Ni coatings offer better corrosion resistance than *B*-Zn-Ni and Cd coatings. It has been attributed to the formation of corrosion products which helps in increasing resistance to further corrosion. Based on the results, it appears that Cd-Ti coating also fares well, ignoring its health hazard. Figure 27(B) provides the changing resistance to corrosion with time due to the formation of protective corrosion products mentioned above. The figure shows the plots for different coatings from initial, 4 h, and 24 h the exposures to the corrosive environment. The response of the *D*-Zn-Ni coatings seems to be better than the other coatings.

The author concluded from his study that lower corrosion rates in Zn-Ni coatings than Zn and Cd coatings. The polarization resistance of Zn-Ni coatings is higher than Zn or Cd coatings. *D*-Zn-Ni coatings showed higher polarization resistance. It is possibly related to the morphology of the coatings and initial dezincification that helped form a strong adherent corrosion product. It helped in providing further resistance to corrosion, as Figure 27(B) after 24 h exposure has shown.

Sriraman also has done tribological aspects with or without the corrosive media, which we will not be discussing here, and the reader is referred to his original thesis for more details. The only thing that is lacking in his study is the evaluation of the hydrogen embrittlement or re-embrittlement of the *B* and *D* coatings in relation to Cd coatings in terms of sustained load crack growth or corrosion fatigue. Hopefully, this will be done in the future.

Figure 27: Comparison of corrosion resistance by different coatings as measure by EIS and plotted as Nyquist plots. (A) Comparison of B and D Zn-Ni plating with LHE Cd and Cd-Ti electroplating. (B) Changes in the corrosion resistance as a function of time as corrosion products form, providing further corrosion protection. From Sriraman (2012).

3.5 Other improvements to the Zn-Ni coatings

3.5.1 PVD Zn-Ni coatings

Other alternate methods of depositing Zn-Ni coatings were attempted since the electroplating contributes to hydrogen emission, dissolution, and subsequent hydrogen embrittlement. For example, Bowden and Mathews (1995), have studied in the past, Zn-Ni coatings using the physical vapor deposition technique (PVD) technique. They tried depositing 10 and 12 wt. % Ni and the graded composition of Ni with Zn using the PVD technique on high-strength steel. They compared their corrosion behavior with PVD Zn and PVD Cd and electroplated Zn-Ni coatings with 12% wt. Ni. C.

Coatings deposited to a thickness of $1 \mu\text{m}$ were used for electrochemical corrosion studies. All tests were carried out at 25°C using a 5% NaCl ($\text{pH} = 6.3$). For the linearization, resistance sweeps 0.28 cm^2 coating area was exposed to an aerated NaCl solution in a three-electrode cell, with the platinum electrode and SCE reference. Potentiodynamic polarization sweeps were made for each of the coatings exposed to 5% NaCl solution. The polarization resistance was determined by calculating the slope of E versus $\log i$ plot from the sweeps on each coating.

In Figure 28, the polarization curves generated using a corrosive electrolyte medium are presented. The Tafel's extrapolated values of E_{corr} and I_{corr} values are also shown in Table 5 for comparison. They found that PVD Zn-12% Ni deposits have the lowest corrosion rate. From the corrosion protection point, they are better than the electroplated Zn-Ni coatings. However, since their electrode potential is higher

than that of the electroplated Zn-Ni coatings, they concluded that they are not ideally suited as the sacrificial coatings for steels. There were not any reported follow-up studies of PVD coatings of Zn-Ni coatings after the above study.

3.5.2 Addition of the third element to Zn-Ni coating for improvement

Recognizing that Zn-Ni coating is an excellent substitute for Cd coatings, there have been some efforts to experiment by adding a third element to improve its performance

Figure 28: Comparison of polarization curves of electroplated Zn-Ni with physical vapour deposited Zn-Ni with Ni 10–12 wt. %, and Cd coatings and of uncoated steel. Measurements were made using a three-electrode cell, with a platinum electrode and SCE reference. The coating thickness is around $1 \mu\text{m}$. From Bowden and Mathews 1995.

Table 5: Comparison of PVD versus electroplating coatings with respect to corrosion potential and corrosion current by Tafel's extrapolation (from Bowden and Mathews 1995).

Coating	Corrosion potential E_{corr} (mV)	Corrosion current i_{corr} ($\mu\text{A}/\text{cm}^2$)
Bare steel	-603	7.8×10^{-4}
Pure Cd	-770	5.1×10^{-5}
Zn-Ni electroplate	-865	5.7×10^{-5}
Zn-Ni-PVD 12%Ni	-615	9.5×10^{-6}
Zn-Ni-PVD 10%Ni	-679	2.2×10^{-5}
Zn-Ni-PVD graded comp	-800	2.5×10^{-5}
Pure Zn	-1310	3.8×10^{-4}

further. Dorairajan et al. (2000), for example, tried to add Cd to the Zn-Ni coatings. They consider that Zn-Ni with 14 wt. % Ni with high Zn content is more electronegative than cadmium. Hence, it is expected to get dissolved rapidly in corrosive environments. They experimented by addition Cd to the coating by adding cadmium sulfate to the electroplating solution. They show that Zn-Ni-Cd coatings have superior corrosion resistance and barrier properties than the typical Zn-Ni and cadmium coatings. They have done polarization studies and electrochemical impedance spectroscopy analysis on Zn-Ni-Cd coatings. They show a barrier resistance that is 10 times higher than that of a conventional Zn-Ni coating, see Figure 29. Dorairajan et al. (2000) report that the corrosion studies of

Zn-Ni-Cd coatings were carried out in a 0.5 M Na_2SO_4 + 0.5 M H_3BO_3 buffer solution of pH 7.0. A three-electrode setup and an EG&G PAR model-273 potentiostat, and a Solatron impedance analyzer were used to perform the corrosion measurements. A standard calomel electrode (SCE) was used as the reference and a platinum mesh electrode as the counter electrode. The average thickness of the coatings is about 15 μm .

They show that the corrosion current is one order of magnitude smaller for Zn-Ni-Cd, obtained by adding 3 g/l CdSO_4 to the bath, than that of pure cadmium coating. The corrosion resistance curve in terms of the Nyquist plot, Figure 29(B), compares the performance of different coatings. Increasing CdSO_4 concentration from 0.5 to 3 g/l enhanced the corrosion resistance. They found that the concentration seems to be optimum since no further improvement occurred by increasing the sulfate concentration. These results show that the performance of the Zn-Ni coatings can be further improved by adding a third element to the coating.

Considering Cd addition is a health hazard, several other attempts were made to add a different third element to the Zn-Ni coatings to improve its performance. The addition of Co, for example, is considered. Co is a part iron triad group that consists of Fe, Co, and Ni due to their similar properties and being close to each other in the periodic table. Figure 30 provides the polarization behavior and Nyquist plot of corrosion resistance of the Zn-Ni-Co electroplated coatings from Eliaz et al. 2010. The

Figure 29: (A) Performance of the polarization behavior of Zn-Ni-Cd coating in relation to just Cd coating. The average thickness of all coatings is about 15 μm . A standard calomel electrode (SCE) was used as the reference. (B) Nyquist plot showing corrosion improved corrosion resistance with the addition of Cd to Zn-Ni coatings. Adding a higher concentration of CdSO_4 (from 0.5 to 3 g/l) improved the corrosion resistance of the coating further. The percent of Ni in the coating is reduced by the addition of Cd to the coatings, although the actual percentages of each element were not determined, see Dorairajan et al. (2000).

potentials were measured using a saturated calomel reference electrode (SCE). The aqueous corrosion behavior of the coatings was studied by the potentiodynamic polarization and EIS techniques. The corrosion current density and corrosion potential were determined based on Tafel's extrapolation. The exposed surface area of all samples was 1 cm^2 . A standard three-electrode cell containing 5% analytical grade NaCl at 25°C was used. The potential was measured versus SCE, whereas Pt mesh was used as a counter electrode. An Electrochemical Work Station (PGSTAT 30 from Metrohm) was used and applied a scan rate of 1 mV s^{-1} , from -0.5 V versus open-circuit potential (OCP) to $+1.0 \text{ V}$ versus OCP. The EIS measurements were run from 100 kHz to 10 mHz , and the Nyquist plots were analyzed. While the thickness of the coatings depends on the current density, the average thickness of the coatings is around $25 \mu\text{m}$. The authors state that approximately Zn-Ni has 10 wt. % of Ni, and Zn-Ni-Co has 8 wt. % of Ni and 4 wt. % of Co, and Zn-Co has 10 wt. % Co. They have compared the performance of Zn-Ni-Co with those of binary Zn-Ni and Zn-Co electroplatings. While the polarization curves for Zn-Ni and Zn-Co coatings are close, Figure 30(A), Zn-Ni-Co curves show that the electrode potential is less negative, with the higher corrosion resistance and lower sacrificial character of the coatings. Generally, the sacrificial nature of the coating is related to Zn-rich solid solution phase (generally referred to η -phase) and the barrier protection to γ -phase (See Figure 17 – phase diagram). During the coating, the inner layers contain the Ni- or Co-rich γ -phase while the outer layers contain Zn rich phase, thus providing sacrificial and barrier protection. The authors claim that the η -to- γ ratio was lower in the

ternary coating containing Zn-Ni-Co, thus accounting for the lower corrosion rate in the ternary alloy.

The EIS data, providing the Nyquist plot, helps rank the coatings by assessing the interfacial reactions and their nature by quantifying the coating breakdowns. Figure 30(B) shows the corrosion resistance of the ternary coatings in 3% NaCl solution. The results are compared with those of binary Zn-Ni and Zn-Co coatings. The authors attribute the improved corrosion resistance of the ternary to several factors. These include a) the unique surface chemistry with higher oxygen content, b) η -to- γ ratio changing with the thickness of the coating, c) surface morphology with reduced surface roughness, etc., besides the intrinsic electrical properties of the coating surface.

Experiments were also done by adding a non-metallic as the third element to the Zn-Ni coatings. For example, Constantin (2014) more recently evaluated the effect of adding phosphorus to the Zn-Ni coatings to improve its performance in protecting the substrate steel. Furthermore, he used an electroless-coating process for Zn-Ni-P coatings. The electroless deposition process involves the autocatalytic reduction of metals. It is a chemical deposition process by using an oxidizing agent. By that method, he deposited Zn-Ni-P coatings using sulfate and chloride solutions. The average coating thickness was around $7.5 \mu\text{m}$. Corrosion studies were performed on the deposited samples using a PARSTAT 2273 potentiostat. The tests were done in 3.5% NaCl aqueous solution at a 25°C temperature in a three-electrode electrochemical cell. The steel samples coated with the electrolessly deposited thin film constituted the working electrode, and a platinum sheet was used as the cell counter electrode. A saturated calomel

Figure 30: Modification to Zn-Ni Coatings to improve coating performance by adding Co. (A) Polarization curves, (B) corrosion resistance curves in terms of Nyquist plots. On the average thickness of the coatings was around $25 \mu\text{m}$. Similarly, Zn-Ni has 10 wt. % of Ni, and Zn-Ni-Co has 8 wt. % of Ni and 4 wt. % of Co, and Zn-Co has 10 wt. % Co. The potentials were measured using SCE standard. From Eliaz et al. (2010).

electrode was used as a reference electrode. The working electrode potential scanning rate was 0.166 mV/s.

Polarization curves for selected Zn–Ni–P coatings are given in Figure 31. Table 6 below provides the exact composition of the coatings along with **Tafel's** values. While the deposits could give enhanced corrosion resistance, their suitability as sacrificial coatings were not studied in relation to electroplated Zn–Ni coatings and their cost-effectiveness for structural steels.

Electroless bath details are given below.

All baths have a gallon of water 40 g of NiSO_4 , 10 g of NaH_2PO_2 , 1 g of $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$, and 50 g NH_4Cl . The only difference between the three baths is the amount of ZnSO_4 . Bath A contains 5 g, bath B has 10 g, and bath C has 20 g. The wt. % of Zn in the coatings increased with the increased amount of ZnSO_4 in the bath.

Based on the extensive work on the electroplated Zn–Ni coatings, we can conclude that Zn–Ni electroplated coatings containing 14%Ni are ideal for a sacrificial coating on high-strength steel. More recent efforts, however, were tuned to how to improvise these coatings further. These efforts led to the development of compositionally modulated multilayer coatings (CMML) of Zn–Ni that will be discussed next.

3.5.3 Compositionally modulated multilayer coatings

Further improvements in the performance of electroplated Zn–Ni coatings are being achieved by exploring the advanced coating technique, which is now called compositionally

Figure 31: Polarization curves for the electroless thin film coatings of Zn–Ni–P. The average coating thickness was around 7.5 μm . A saturated calomel electrode was used as a reference electrode. See text for details of the composition of the coatings and Tafel's values. From Constantin (2014).

modulated multilayer (CMML) coatings, also referred to as compositionally modulated multilayer alloy (CMMA) coatings. Initially, two separate baths were alternately used to obtain multilayers. Later, it was found that one can achieve CMML by using a single bath but alternately changing the current densities between two selected values. Multilayers, with the thickness of each layer in the range of nanometers, can be obtained by cycling current density strictly between two levels and selecting the duration time at each level. Each layer could be of nanosize, with the total thickness of all the layers the same as the monolayer coating. In many coatings, significant improvements in the performance of the coatings can be achieved through CMML. By controlling the coating parameters, CMML can have a) improved mechanical strength or hardness, b) controlled diffusion of hydrogen, c) enhanced ductility and toughness, d) reduced density, e) controlled thermal expansion coefficient, and f) most importantly, enhanced corrosion and wear resistance depending on the nature of the coatings employed. Figure 32, for example, provides some advantages of multilayers in contrast to monolayer coatings. Figure 32(A) shows the sequence of changing current density to obtain alternating layers. Figure 32(B) describes how each layer can act as a fresh layer in protecting the substrate while still acting as the sacrificial layered coating.

The coating thickness, composition, texture, the microstructure depends on the current density, stirring speed, etc., besides the bath composition and the additives. Hence optimum coatings conditions, including the number of layers required, must be arrived at by trial-and-error approach. Extensive work has been done on CMML Zn–Ni coatings by Prof. Chitharanjan Hegde's group of the National Institute of Technology, Karnataka, India. Some relevant papers of his group are listed in the references, Bhat and Hegde (2011), Bhat et al. (2011), Hedge and Thangaraj (2009), Thangaraj et al. (2009).

As discussed above, the periodic change in the current density (CD) causes the formation of layers, and the time at each CD controls the thickness of each layer deposited.

Table 6: For different coatings, electroless baths, coating thickness, chemical composition, and the electrode potential of the coating with the substrate are given.

Coating	Bath & time	Coating thickness (m)	Zn wt. %	Ni wt. %	P wt. %	E_{corr} (mV)
Base						–619
ZnP-2	A/2 h	8.5	8.89	89.38	3.07	–562
ZnP-4	B/2 h	7.9	14.73	77.79	7.48	–479
ZnP-6	C/2 h	8.8	40.65	53.02	6.33	–389

Figure 32: (A) Compositionally modulated multilayer coatings can be obtained using a single bath by alternating between two current density (CD) values X and Y . (B) Shows each layer can act as independent in protecting the substrate and as a diffusional barrier. Figure B is adopted from Rashmi et al. (2017).

Associated with a change in the layers is also a periodic change in the chemical composition. Zn–Ni coatings have been found to cause ‘anomalous codeposition with percent of Zn decreasing and Ni increasing with an increase in current density. Hence a periodic change in CD also changes the Zn–Ni ratio with each layer. Since the composition changes with the CD, the composition of the multilayers can be modulated using appropriate changes in the CD for a given bath.

Venkatakrishnan and Hedge (2010) have evaluated the corrosion resistance of Zn–Ni’s CMML coatings, using several two different sets of periodic CD levels on the substrate steel. They controlled the thickness of each layer by the duration of the plating time at the selected CD. The coating composition varies with CD. Generally, for the purpose of the study, the thickness of each deposited layer was maintained to be around a few nanometers. The total number of layers was controlled by the number of times the selected CD values are changed and coating time at each CD level. A SCE was used for measuring potentials. The corrosion studies were carried out at 25 °C in 5% NaCl solution at pH 6.0, prepared in distilled water. Cathodic and anodic polarization curves were obtained at a scan rate of 1 mV s^{-1} by using SCE as a reference and platinum electrode as a counter. The impedance behavior of the deposits was studied by drawing the Nyquist plot in the frequency range from 100 kHz to 10 MHz. They found that the performance of CMML layers using a) periodic sets of 20/40 mA/cm^2 CDs are the best followed by 20/50 set, b) maximum of 120 layers provide the best corrosion resistance. Further increase in the number of layers beyond 120 resulted in decreased resistance, Table 7. Further increase in the number of layers resulted in the uneven distribution of the

Zn and Ni due to limited time during deposition. In essence, the CMML coatings need to be optimized for given bath conditions in terms of CD levels, the time at each CD level, and the number of periodic changes to obtain the optimum number of layers and thickness for maximum protection of the steel. Figure 33 shows the polarization curves and Nyquist corrosion resistance curves for different number layers of Zn–Ni coatings deposited using the periodic 20/40 CD levels. They show that corrosion resistance of 120 CMML layers provided nearly 60 times better than the monolayer when the total thickness of the two coatings the same. Thus, the compositionally modulated multilayer coatings using the stepwise periodic changing of current densities seem to have a quantum improvement in Zn–Ni electroplating sacrificial coatings.

Maciej et al. (2012) have done a more independent evaluation of Zn–Ni CMML coatings made again using a single bath, but by cycling current density between 2 and 4

Table 7: Effect of CCML coatings on the corrosion properties Zn–Ni coatings.

Coating CD cycle	Number of layers	E_{corr} (V)	i_{corr} (A/cm ²)	Corrosion rate ($\times 10^2 \text{ mm/Year}$)
Monolayer (Zn–Ni)	1	–1.142	14.91	21.4
	6	–1.125	4.404	6.34
CD20/40	20	–1.214	1.246	1.79
	60	–1.169	0.383	0.55
	120	–1.049	0.253	0.32
	120	–1.084	12.664	18.23
(Zn–Ni) CD 20/50	6	–1.084	12.664	18.23
	20	–1.146	2.188	3.15
	60	–1.112	0.571	0.82
	120	–0.998	0.276	0.5

Figure 33: Zn-Ni compositional modulated multilayer coatings. (A) polarization curves, (B) Nyquist corrosion resistance plot. The saturated calomel electrode (SCE) was used as a reference for measuring potentials with Pt electrode as a counter. From Venkatakrishnan and Hedge (2010).

A/dm² and compared with monolayer coatings deposited at the above CDs. The evaluation was done by depositing mono or multilayer coatings of the same net thickness. 2, 4, 50 layers coatings all of 16 μm thick were made. Chemistry, microhardness, corrosion potential, and corrosion rate were evaluated using the appropriate tools. The corrosion resistance of the alloy coatings was investigated using a potentiodynamic polarization method. Measurements were performed with a scan rate of 1 mV s⁻¹, at a temperature of 25 °C in a 5% sodium chloride solution with free access to air. A typical electrochemical cell in a three-electrode configuration with a SCE as the reference electrode and platinum gauge as a counter electrode were used in the electrochemical measurements.

The authors have done the coatings evaluation tests using the ASTM test criteria as the basis. Figure 34 shows the polarization curves for 2, 4, and 50 layers of CMML coatings and compares them with the curves of monolayer coatings plated at 2 and 4 CD coatings. The total thickness of all the coatings was kept the same (16 μm) for the comparison to be valid. Tafel's extrapolated E_{corr} and I_{corr} values from the polarization data for all coatings are provided in Table 7, along with the results of the corrosion test. The authors claim that the coatings were dense and adherent and were of uniform thickness. The compositional variation between adjacent layers was limited to 2 wt. % with cyclic changes in the Zn and Ni contents.

Hegde and his group have shown that CMML Zn-Ni coatings are superior as sacrificial coatings than the monolayer coatings. Rao et al. (2013) have studied the thermal stability of these CMML coatings. The corrosion behavior of the coatings was evaluated in 5% NaCl solution

at pH 4.0 using Potentiostat/Galvanostat at a temperature 25 °C, using a saturated calomel electrode (SCE) as a reference, and platinum as counter electrodes. The coating thickness was around 15 μm. They have shown first that the composition of the Zn-Ni coatings can vary with the current density used for plating for a given bath. Table 8 below shows a) the relative concentration of Zn and Ni vary by changing current density even for monolayer coatings and b) the associated changes in the potentiodynamic polarization values, and c) the corrosion resistance of the coating. The authors used a current density of 3 A/dm² charge density for their CMML coatings based on these results. Their work shows that it is essential to investigate a given electrochemical plating solution with the best current density and stirring speed that gives the optimum coating protection.

Rao et al. also evaluated the thermal stability of the multilayer coatings. Since each layer is nanoscale, for 300 layers, the interfacial energies involved are expected to be significant, contributing to their instability. The coatings were heated to selected temperatures for 1 h, and subsequent properties were evaluated. It is done for both monolayer coatings deposited at 3 A/dm² and CMML 300-layer coatings deposited using the periodic CD of 2 and 4 A/dm². Figure 35(A) gives the polarization curves for CMML 300 layer and monolayer coatings before and after heat treatment at 100 °C. The Tafel's extrapolated E_{corr} and i_{corr} values are provided in Table 9. The corrosion resistance of the coated steel is also investigated in corrosive electrolytes and plotted using Nyquist plots in Figure 35(B). These results indicate that CMML 300-layer coatings performed better than the monolayer coatings, further confirming compositionally

Figure 34: CMML coating of Zn–Ni using periodic 2 and 4 CD cycles to obtain a different number of layers, all of the same total thickness of 16 μm . (A) shows the polarization plot of 2, 4, and 50 layers, with a saturated calomel electrode (SCE) as the reference electrode and platinum gauge as a counter electrode used in the electrochemical measurements. (B) The current density cycles used to get CMML coatings. From Maciej et al. (2012).

Table 8: Comparison of corrosion potentials, current, and corrosion rate of monolayer versus multilayers with composition modulation by cycling current density during plating (from Maciej et al. 2012).

Number of layers	E_{corr} (V)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mm/year)
Zn	−1.011	25.2	0.363
2CD – Mono layer	−0.959	4.03	0.058
4CD – Mono layer	−0.937	2.90	0.041
2-Layers	−0.937	2.16	0.031
4-Layers	−0.965	3.98	0.057
50-Layers	−0.964	2.33	0.033

Table 9: Changes in the wt. % Ni in the Zn–Ni coatings with changes in the current density along with corresponding changes in the potentiodynamic polarization values and corrosion resistance of the coatings.

Current density (A/dm ²)	Wt. % Ni	E_{corr} (V)	i_{corr} (A/cm ²)	Corrosion resistance (mm/year)
1.0	2.62	−1.019	17.62	23.42
2.0	4.05	1.086	13.87	18.44
3.0	7.95	−1.105	10.88	14.66
4.0	8.07	−1.162	12.53	16.66

Figure 35: (A) Polarization curves of Zn–Ni CMML coatings with 300 layers in comparison with a monolayer of the same thickness (15 μm) made using the same electrolyte bath. They have used saturated calomel electrode (SCE) as a reference, and platinum as counter electrodes. The effect of 100 $^{\circ}\text{C}$ on the polarization curves is also shown. (B) The corrosion resistance of the coatings using Nyquist plots. From Rao et al. (2013).

Table 10: Effect of heat-treatment temperature on the properties including corrosion resistance of 300-layer CMML coatings in relation to those of monolayer coatings.

Current density (A/dm ²)	Heat treatment temperature (°C)	Coating thickness (μm)	Vicker hardness (V100)	E_{corr} (V)	i_{corr} (μA/cm ²)	Corrosion resistance (×10 ² mm/year)
300 layers	30	18.9	212	−1.003	0.31	0.41
	100	16.7	189	−1.022	2.14	2.84
	200	14.3	183	−1.024	2.18	2.89
	300	9.1	154	−0.995	3.73	4.95
	400	5.4	139	−0.865	4.52	6.0
Mono layer	30	17.8	202	1.128	10.78	14.33
	200	9.3	145	−1.053	21.68	28.82
	400	4.8	119	−1.070	26.53	35.27

modulated multilayers are superior in terms of their performance in protecting the substrate steel (see Table 10).

3.5.3.1 Hydrogen embrittlement and re-embrittlement

While an extensive study has been done developing compositionally modulated multilayer coatings as summarized above, there has not been any reported work related to the hydrogen embrittlement and re-embrittlement under monotonic and cyclic loads. These are important for structural applications. Since electroplating always involves hydrogen emission that contributes to hydrogen embrittlement, evaluating the stability of the coatings under monotonic and cyclic loads is essential for any coating development. While the analysis above indicates that CMML coatings provide better coatings than monolayer coatings, there is a need to evaluate their hydrogen embrittlement under monotonic and cyclic loads and their tribological properties. The studies should also include the need and the role of post-baking after coating to remove any damaging hydrogen.

4 Summary and conclusion

An extensive review of the Zn–Ni sacrificial electroplating of high-strength steels and their stability under hydrogen embrittlement has been provided. The review starts from the early work to the latest compositionally modulated electroplated coatings. Hydrogen embrittlement becomes an intrinsic limitation of these coatings since hydrogen emission is unavoidable during electroplating. These high-strength steels are being used in a corrosive environment, and most of the crack tip delayed crack growth occurs either from the internal hydrogen or external hydrogen arising from the corrosive crack-tip reactions. Therefore, it becomes essential to evaluate these coated steels under monotonic loads using slow strain rate tests or under cyclic

loads under different load ratios. The current analysis included not only research results done at universities but also under special research programs sponsored by the Navy, the results of which are available online. Based on the review, we conclude that the compositionally modulated multilayer coatings of Zn–Ni appear to be best suited as sacrificial coatings. Further experiments should focus on their susceptibility for hydrogen embrittlement and sacrificial protection under applied stresses in corrosive environments encountered in service. Perhaps a suitable Navy program needs to be developed for the industrial application of these compositionally modulated multilayer Zn–Ni coatings, as was done before.

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