Designing Composition Band for Zn-Ni Electroplating Deposits on Steel Panel Substrates to Mitigate Stress Corrosion Cracking

(Technical project)

Identifying Pitfalls in Regulating Cadmium Use and Emissions

(STS project)

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On my honor as a University student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments.

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Introduction

Corrosion is the process of environmental exposure causing reactions which remove material from the surface. This happens spontaneously to metals when exposed to water, as a common example, which together experience electrochemical reactions reversing the metals to a state similar or identical to their mineral forms (Jones, 1996, p. 5). Atoms from the metallic surface dissolve into metal cations, and the free electrons produced in this reaction are consumed by reactions with hydrogen ions and dissolved oxygen (and other cations in the solution such as sodium in salt water). Rust in iron and steel alloys is one example of corrosion, and enough surface damage eventually leads to mechanical failures. The damage caused by corrosion and the countermeasures for resisting it cause enormous economic costs (Jones, 1996, p. 3-4).

Environmental coatings are used to protect metals from corrosion by serving as a barrier on the surface. A passivating coating protects by being relatively unreactive. Sacrificial coatings protect by instead corroding more spontaneously. One example of the latter is electroplated cadmium coatings which have served as an effective industry-standard sacrificial coating for salt-water environments with good mechanical properties (ChemResearch Co, 2023). However, cadmium is a carcinogenic heavy metal which increases cancer risk in exposed individuals, particularly in those working directly in industries involving its use (IARC, 2012; Mead, 2010). Studies on the negative effects of cadmium exposure have prompted industry and government regulations to reduce cadmium concentration in the environment due to cadmium coatings and other industries.

To remove one source of artificial cadmium emission, less toxic materials such as zinc-nickel (Zn-Ni) alloys are being developed as replacements for environmental coatings. Zinc alone can serve as a sacrificial coating but is too reactive, so zinc is alloyed with nickel to improve its coating resistance (Farooq et al., 2022). Zn-Ni alloys can be made with corrosion resistance matching that of cadmium, but being an alloy means that the composition needs to be carefully controlled to provide adequate corrosion resistance, balancing passivating and sacrificial behavior, as well as good mechanical performance (Sabelkin et al, 2016; Logan, 1952, p. 99-105).

Current research and development of Zn-Ni coatings prompts two major questions about replacing cadmium coatings. First, how can Zn-Ni coatings be engineered to perform at least as well as cadmium for sacrificial corrosion protection? Second, given that cadmium's toxicity was first studied decades ago, why has it taken so long to adequately regulate and replace cadmium usage? To address engineering problems with Zn-Ni, the technical team will research processing parameters for finding optimal alloy composition and reducing its variation, which is expected to include a new postprocessing procedure for selectively reducing zinc content at the surface. The broader sociotechnical issue will require a literature review of studies on cadmium's toxicity as well as past and current regulations for mitigating cadmium exposure and related news coverage, looking for root causes of slow action on this aspect of protecting human and environmental health.

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Zinc-nickel coatings provide corrosion protection in almost an identical way to cadmium in that it provides a sacrificial coating to protect against corrosion and is applied via electroplating. Zinc is the sacrificial element within the coating, but on its own it corrodes too easily. This is why the coatings are alloyed with 12-15 wt% nickel to slow the zinc's activity, reducing the corrosion rate compared to pure zinc by a factor of four (Farooq et al., 2022). Dezincification occurs above 15 wt% Ni, causing the alloy to lose sacrificial properties as the alloy becomes more noble than the steel substrate. Plating tank conditions are therefore carefully monitored to ensure the optimum mix is maintained. In cadmium, the corrosion behavior is relatively uniform and homogenous. However, in Zn-Ni, corrosion is not uniform in terms of rate or location (Vierra et al, 2009). This inconsistency is something that needs to be identified and reduced for optimization.

One significant problem in environmental barrier coatings is stress corrosion cracking (SCC), where the electrochemical reactions of corrosion combined with mechanical stress in the material cause cracks to form. SCC occurs due to a combination of chemical and mechanical factors allowing for crack propagation under conditions where purely mechanical or chemical action would not occur. Crack nucleation often begins at surface discontinuities such as from fabrication, surface damage, and corrosion pits from uneven dissolution, and over time SCC contributes to this localized damage until the whole component fails. (Jones, 2017). SCC can occur in any metal; however, alloys are particularly susceptible in part because different elements corrode more favorably (Jones, 1996, pp. 237-238). To reduce SCC in environmental coatings such as Zn-Ni, engineers want to electrocoat the coating in such a way that it is both reasonably resistant to corrosion and has a consistent composition throughout the coating of the ideal weight percents of each element.

Conceptual design for this project has produced many different avenues for approaching a solution; should the team seek to electrodeposit Zn-Ni coatings onto a steel substrate using UVA facilities, many tunable parameters would then in play such as current density, bath chemistry and temperature, coating thickness, and electrochemical setup. These parameters contribute to the kinetics behind the electrodeposition and impact the weight fractions of zinc and nickel as well as the phases and microstructure (Conde et al., 2011; Kanani, 2004; Qiao et al., 2013; Conrad et al., 2011). Pursuing electrodeposition would require eliminating variation in all parameters to identify which parameters in electrodeposition have the most predictably incremental and tunable results.

The objectives of this project are to determine the optimal Zn-Ni concentration to achieve balanced properties within a range of 12-15 wt% Ni and develop a +/- 0.25 wt% tolerance band of Ni content in a Zn-Ni electroplated deposit on steel panel substrates with the intention of mitigating stress corrosion cracking in high-stress field conditions. We plan to accomplish this by introducing a post-processing step of selectively leeching Zi from the coatings, putting current through the material to intentionally corrode Zi from samples to increase the Ni wt% to target composition. This preferential dissolution will increase the ratio of Ni in the coating, increasing the nobility of the coating to be within an immunity region where SCC will not occur. This will require experimentation to identify the parameters needed for a procedure usable by industry such as Rolls-Royce who could then adapt their Zn-Ni coatings for better performance.

Identifying Pitfalls in Regulating Cadmium Use and Emissions

Cadmium corrosion-resistant coatings are effective, but they are being phased out due to concerns about the metal's toxicity. Cadmium coating has been used to protect steel from corrosion for decades due to its numerous protective properties including exceptional corrosion resistance, increased lubricity, better chemical resistance, improved ductility, excellent solderability, and high electrical conductivity. Most notably, cadmium is highly resistant to corrosion from salt water, a characteristic of great interest to the aerospace and defense industries. The European Union has banned cadmium use, and its use is heavily limited to certain applications in the United States (ChemResearch Co. 2021). There is an increased interest in implementing electrodeposited Zn-Ni sacrificial anodic coatings in its place because they are non-toxic and have a very similar degree of corrosion protection. As a cadmium replacement, Zn-Ni provides many of the other same benefits. As well as providing excellent corrosion protection, Zn-Ni also provides excellent coverage and thicknesses in comparable ranges. It also boasts high hardness and is resistant to high temperatures, both of which are considerable improvements over soft and much less heat resistant cadmium.

Cadmium is a naturally occurring element, but it can appear in dangerous concentrations after corrosion and there's no mechanism for cadmium degrading naturally (Shacklette, 1972). There have been several incidents of product recalls on account of excess cadmium such as a McDonalds drinking glass and several lines of toy jewelry. There is also cadmium generated through ore smelting and fossil fuel use as well as food-related sources such as phosphate-based fertilizers and shellfish aquaculture (Mead, 2011). Several case studies suggesting that cadmium exposure leads to increased cancer rates such as in lungs and prostate, including animal experiments on rodents exposed to cadmium through ingestion and inhalation which found increased occurrences of various forms of cancer and several mechanisms from literature for how cadmium damages DNA and disturbs DNA-repair and tumor-suppressing proteins (IARC, 2012).

Cadmium has been studied as a substance present in daily intake through inhalation and ingestion as early as the 1970s (Friberg, 1971, pp. 24-33). This stems from research going as far back as 1858 with one study on acute gastrointestinal and delayed respiratory symptoms among users of cadmium carbonate powder, and starting with one experimental toxicology study in 1919, several animal experiments and case studies throughout the 20th century found cadmium and cadmium-containing compounds to be damaging to tissue (Nordberg 2009; Pařízek, 1957; Miller et al, 1969). Despite the research body on cadmium toxicity, it was not until 1979 that Sweden passed one of the first cadmium bans, and even then, they delayed the ban's enactment until July 1, 1982 following an overwhelming number of applications for exemptions (Nilsson, 1979; Hinrichsen, 1980). The European Union added cadmium use in jewelry and plastics to the substances banned under the Registration, Evaluation, Authorization & Restriction of Chemical substances (REACH) chemical law as of late 2011 (Erickson, 2011). To this day, scientists perform studies on the health implications of cadmium exposure and legislators attempt to regulate its use and emissions (Sovičová et al, 2019; "Minnesota, USA, Regulates Chemicals in Products," 2023).

Despite research on health risks of cadmium exposure beginning over a century ago, government and industrial interests have only enacted regulations in recent decades and still have allowed notable instances of cadmium exposure. In this study, I intend to research why it has taken so long to establish meaningful regulation to protect people from excessive cadmium exposure. This research will build off Trevor J. Pinch and Weibe E. Bijker's social construction of artifacts: a Social Construction of Technology (SCOT) approach is necessary for considering the interconnectedness of the places cadmium appears and the stakeholders between industry, government, and the consumers (Pinch and Bijker, 1984, p. 410-412). The main source of information will come from reviewing literature pertaining to cadmium use in engineering products, research on cadmium toxicity, and government documentation (and related news) in the United States and European Union covering cadmium regulation and bans, which will allow me to construct a complete timeline of cadmium use and regulation and identify which industries have had the most influence. It may be more difficult finding sources for going farther back in time due to availability. It will be possible to identify the key reasons why industry and government legislation has come so much later than scientific understanding on cadmium's toxicity to humans.

Conclusion

The Zn-Ni postprocessing research is expected to yield data on the corrosion resistance of the coatings accompanied by a procedure for optimal zinc removal. Industry interests such as Rolls-Royce could adapt this research to help make replacements for cadmium coatings more viable. The findings of the STS research should highlight the notable flaws in the implementation of policies relating to cadmium, which hopefully will inform future health and environmental policy and how to avoid previous shortcomings. Together, the outcomes of these projects will demonstrate how replacing cadmium use in safer coatings, and engineering products more broadly, is both possible and necessary for protecting public health.

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