Background

Hydrogen permeation and related stress corrosion cracking (SCC) can limit the use of metals and alloys in aqueous environments. The interactions between hydrogen and the heterogeneities in the microstructure initiate the events leading to a crack. Various methods like the post-heat treatment, alloying, laser surface modification and shot peening have been proposed to decrease hydrogen permeation. These methods however, do not reduce the hydrogen entry below the threshold level that is safe of cracking hazards. On the other hand, coating the hard alloy with a suitable metal/alloy can successfully reduce the hydrogen ingress into the metal. The coatings can either be metallic or may consist of metallic particles bonded with an inorganic matrix, often phosphates and/or chromates. An important requirement, however, is that the coating should provide sacrificial protection if the substrate becomes exposed.

Cadmium plating is widely used for the protection of aircraft components, which are made from steel. Cadmium electroplate on steel has many advantages such as good lubricity, solderability, low galvanic corrosion with aluminum. Cadmium plating offers an effective barrier protection to the substrate especially in the marine environment. Cadmium also offers sacrificial protection to the steel components under corroding conditions. Cadmium is predominantly deposited using a cyanide bath, the disposal of which is a problem. Consequently, efforts have been made world wide to develop an alternate to cadmium coatings. Several research groups, all over the world, have contributed significantly to this development. The Center for Electrochemical Engineering at the University of South Carolina (USC) has partnered with Office of Naval Research (ONR) and American Electroplaters and Surface Finishers society (AESF) to research in the area of alternate coatings.

Alternate Coatings

Zinc Coatings

Electrodeposited zinc has been widely used for protection of steel from corrosion. Zinc offers the advantage of being deposited from a wide variety of baths including cyanide bath. We have developed plating techniques for underpotential deposition (UPD) of zinc, which inhibits the discharge of hydrogen on several hard alloys. Deposition of multiple layers of zinc has also been carried out which helps in mitigating hydrogen permeation through hard steel. A drawback with zinc plating however, is the large amount of corrosion products formed and very high dissolution rate of zinc when coupled with iron due to large corrosion potentials of these two metals. Under these circumstances our research has been aimed in developing effective zinc based coating by alloying zinc with a noble metal like nickel.

Zinc-Nickel Alloy Coatings

The current technology available for Zn-Ni plating includes both alkaline and acid plating. Deposit characteristics of Zn-Ni as compared to the conventional zinc include
benefits of extended corrosion resistance and significantly harder deposits. The presence
of nickel also imparts a good barrier resistance to the coating. Deposits obtained using the
acid chloride processes perform better when compared to the coatings obtained using
alkaline processes due to the higher nickel content in the alloy.

The concentration of the alloying metal (Ni) is critical in determining the corrosion
resistance properties of the coatings. Several studies have been done previously to
optimize the composition of Zn-Ni alloys based on corrosion performance analysis.
Typical nickel composition in the Zn-Ni alloy is approximately 10-15% and any further
increase in nickel composition is based on using a higher-than-predicted Ni/Zn ratio in
the bath. An enhancement in noble metal composition would lead to more anodic open
circuit potential, which in turn will reduce the driving force for the galvanic corrosion.
Also the barrier properties associated with such deposits will be superior compared to
other coatings.

We have developed galvanostatic pulse and pulse reversal techniques to electroplate Zn-
Ni alloys in the presence of nonyl phenyl polyethylene oxide (NPPO). NPPO has been
used to increase the nickel content in the alloy and to produce uniform deposits. NPPO
inhibited zinc electrodeposition and acted as a leveling agent as it was seen in our earlier
studies on deposition of zinc and galvanostatic pulse and pulse reverse plating of zinc-
nickel alloys from sulfate electrolytes. We also found that the adsorption of NPPO on the
 electrode surface increased the surface overpotential due to the less effective exchange
current density of the electroactive species participating in the reduction process. At a
specific applied current density, the fractional coverage of the electrode surface with
nonyl phenyl polyethylene oxide causes the operating potential to be extended in cathodic
direction without creating conditions for concentration depletion of the electroactive
species at the interface. The increased polarization under potentiostatic conditions has
also been explained theoretically. Slower kinetics rather than concentration overpotential
compensate for the potential drop, which occurs in the presence of NPPO. We have also
studied the effect of other inert additives like SiO2 in the deposit. Such deposits possess
superior corrosion properties compared to the Zn-Ni alloy. However, the observed small
increase of Ni content in the alloy didn’t improve the Zn-Ni barrier properties.

Zn-Ni-X (X=P, Cu,Cd) Ternary Alloy Coatings

The approach adopted in this work was to develop an electrodeposition process for
plating of Zn-Ni-X (X=Cd,Cu, P) ternary or quaternary alloys, which will induce barrier
properties to the sacrificial Zn-Ni alloy thereby extending the life of the coating. By
introducing a new element in the Zn-Ni alloy one can expect to decrease the Zn-Ni ratio
in the alloy and consequently to decrease the Zn-Ni alloy corrosion potential from –1.14
V vs. SCE to even lower values than the corrosion potential of Cd (-0.79 V) but more
negative than the Fe corrosion potential. Also, by introducing a third element in the alloy
one can modify the rate of hydrogen evolution reaction, the hydrogen proton
recombination and adsorption kinetics at the surface and to impede completely the proton
penetration in the alloy thus eliminating the hydrogen embrittlement.
Alkaline Ni-Zn

Zn-Ni alloy deposition goes through normal and anomalous codeposition based on the applied current density/potential [78]. Normal codeposition of Zn-Ni takes place at low cathodic polarizations and Zn-Ni deposition transforms to anomalous deposition beyond a particular current density/potential [76-78]. The deposits obtained at such low current density and potentials are non anomalous resulting in nickel rich alloys. It has been established that the Ni-Zn alloys with nickel content as high as 72% can be deposited from alkaline sulfate electrolytes. The operating parameters like the concentration of the electroactive species, pH, temperature and applied potential were effectively controlled to yield non anomalous Zn-Ni coatings. The performance of the alloys for corrosion protection of steel has drawn considerable interest in this process.

Electroless Ni-Zn-P sacrificial Coatings

Autocatalytic reduction of metals and alloys offers an attractive and alternate method of increasing the amount of Ni in the final deposit. Electroless deposition has been used to form a thin and uniform Ni-Zn-P film from both sulfate and chloride baths. A novel technique for obtaining non-anomalous Ni-Zn-P coatings with high Ni content (74-wt% as compared to 15-20 wt% in conventional plating method) has been developed. These coatings show promise as a replacement for Cd in sacrificially protecting steel. Varying the concentration of ZnSO$_4$ in the bath controls the final amount of Zn in the deposit. The Zn content in the coating was optimized based on the corrosion resistance of the final deposit. Coatings with 16.2-wt% Zn were found to display a potential of –0.652 V vs. SCE that is more electronegative to steel and hence can be used as a sacrificial coating for protection of steel. Deposition parameters like pH and temperature have been optimized based on composition of the coating and the surface morphology. Ni-Zn-P coatings obtained using the electroless method show a higher barrier resistance and better stability as compared to Cadmium coatings.

Table 1: Comparison of corrosion potential and corrosion rates for different sacrificial coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>$E_{corr}$ (V vs. SCE)</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>Corrosion Rate (x $10^{-10}$ cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-1.123</td>
<td>$1.5 \times 10^{-3}$</td>
<td>39.4</td>
</tr>
<tr>
<td>Zn-Ni</td>
<td>-1.083</td>
<td>$3.8 \times 10^{-4}$</td>
<td>17.7</td>
</tr>
<tr>
<td>Cd</td>
<td>-0.798</td>
<td>$4.0 \times 10^{-3}$</td>
<td>17.2</td>
</tr>
<tr>
<td>Zn-Ni-Cd</td>
<td>-0.640</td>
<td>$9.3 \times 10^{-3}$</td>
<td>6.3</td>
</tr>
<tr>
<td>Ni-Zn-P</td>
<td>-0.652</td>
<td>$8.6 \times 10^{-6}$</td>
<td>3.3</td>
</tr>
<tr>
<td>Ni-Zn</td>
<td>-0.678</td>
<td>$4.8 \times 10^{-6}$</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Sacrificial properties of the coating can be estimated using simple open circuit potential measurement studies. The corrosion potential \(E_{\text{corr}}\) measured indicates the tendency of the metal to corrode in a given environment. By comparing the corrosion potential of two metals, it is possible to conclude which one will corrode. In case of zinc, the dissolution rate is very high due to the high corrosion potential difference between the underlying metal (steel) and the zinc coating. Nickel possesses excellent barrier properties; however, this metal is susceptible to hydrogen embrittlement and cracking.

**Figure 1: Comparison Of Different Deposits in 0.5M \(\text{Na}_2\text{SO}_4\) and 0.5M \(\text{H}_3\text{BO}_3\) buffer solution: \(\text{pH} \ 7.0\ \ T = 25^\circ\ C\)**

The sacrificial properties as predicted by the OCP measurements were verified using the scratch-model approach. The more negative zinc coatings offer high level of sacrificial protection to the underlying steel and inhibit the hydrogen penetration in the bulk of the alloy. However this coating has very short life due to a high rate of galvanic corrosion. The potential of pure zinc was stable at \(-1.1\ \text{V} (\text{vs. SCE})\) whereas, the OCP’s of Zn-Ni, Zn-Ni-Cd, Ni-Zn and electroless Ni-Zn-P were more positive indicating that inclusion of more noble components in the deposit results in the anodic shift in potentials with respect to zinc which in turn decreases the galvanic corrosion.

To evaluate the barrier properties of the coatings, potentiodynamic studies (Tafel and linear polarization) and EIS were performed in an aerated 0.5 M \(\text{Na}_2\text{SO}_4 + 0.5\ \text{M} \text{H}_3\text{BO}_3\) solution (pH 7) at a sweep rate of 0.125 mV/s. Icorr values for any coating can be used along with the equivalent weight to estimate the corrosion rate of the coating in the corroding solution. The corrosion rates were obtained at different times by carrying out the analysis each time on a fresh sample. The corrosion current obtained after 1 hr showed that the zinc coating had the highest Icorr value. The Zn-Ni and Zn-Ni-P coating had higher Icorr values than those found for cadmium suggesting that they will provide
more efficient barrier protection. Zn-Ni-Cd, alkaline Ni-Zn and electroless Ni-Zn-P coatings gave the best performance with stable and significantly lower corrosion current. The $I_{corr}$ observed for these alloys was about one order of magnitude smaller than that obtained for pure cadmium due to the presence of significant amount of nickel in the alloy. Figure 1 summarizes the corrosion rates obtained for different coatings estimated using Tafel measurements. Since the corrosion rate is directly proportional to the corrosion current, the trend remained the same with nickel having the lowest corrosion rate (not shown in fig). Zn-Ni-Cd, alkaline Ni-Zn and electroless Ni-Zn-P has about one order of magnitude lower corrosion rates compared to Zn-Ni, or cadmium coatings. Zinc coating had the highest corrosion rate. Corrosion rates shown in Figure 1 were obtained after 1 hr of immersion in an aerated 0.5 M Na$_2$SO$_4$ + 0.5 M H$_3$BO$_3$ solution (pH 7).

**Hydrogen Permeation Characterization Studies**

Our studies on several coatings indicated that by modifying the electrode surface, one could decrease corrosion and inhibit the subsequent hydrogen permeation. The surface modification has been shown to inhibit the hydrogen discharge reaction or reduce the hydrogen absorption rate causing most of the adsorbed hydrogen atoms to form hydrogen molecules rather than to be absorbed and diffuse into the bulk of the alloy.

The hydrogen evolution and permeation current densities were obtained for Cd, Zn-Ni, electroless Ni-Zn-P and Zn-Ni-Cd deposits. The results are shown in Table 2. The cathodic and permeation current densities were one order of magnitude smaller in case of Zn-Ni-Cd deposits when compared to Zn-Ni deposits while the hydrogen permeation current in case of steel is approximately 2 orders of magnitude higher than that of Zn-Ni-Cd deposits. Zn-Ni and electroless Ni-Zn-P also show good permeation inhibition when compared to steel. Permeation analysis was carried out under different applied potentials in order to simulate the extreme conditions. Table 2 summarizes the permeation data obtained at cathodic overpotential of 300 mV. Maximum reduction in permeation of about 97% was observed for Zn-Ni-Cd alloy as compared to 88% of Zn-Ni alloys.

**Table 2: The different kinetic parameters characterizing the hydrogen ingress through various alloys.**

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Zn-Ni</th>
<th>Electroless Ni-Zn-P</th>
<th>Zn-Ni-Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_0$, A/cm$^2$</td>
<td>6.22 x 10$^{-9}$</td>
<td>6.3 x 10$^{-5}$</td>
<td>4.69 x 10$^{-7}$</td>
<td>9.17 x 10$^{-7}$</td>
</tr>
<tr>
<td>$k''$, mol/cm$^3$</td>
<td>7.32 x 10$^{-5}$</td>
<td>4.11 x 10$^{-5}$</td>
<td>8.74 x 10$^{-7}$</td>
<td>1.11 x 10$^{-5}$</td>
</tr>
<tr>
<td>$k_3$, mol/cm$^2$ sec</td>
<td>1.66 x 10$^{-9}$</td>
<td>5.73 x 10$^{-6}$</td>
<td>1.06 x 10$^{-8}$</td>
<td>0.38 x 10$^{-6}$</td>
</tr>
</tbody>
</table>
The slope of the i-h relationship that is obtained for any particular system decides the selection of an appropriate model that can be used to evaluate the kinetics parameters of hydrogen permeation. It is generally recognized that the overall hydrogen evolution reaction from acid solutions proceeds in two successive stages. The first step, which occurs on all metals, consists of discharge of hydrogen ions and leads to the hydrogen atom adsorption on the electrode surface:

**Schematic diagram of Stachurchi-Devanathan bipolar cell used for evaluating the hydrogen permeation inhibition properties of developed coatings.**

The electrode metal, represented by M, serves as the catalyst. The second step of the hydrogen evolution reaction may involve recombination (chemical desorption), or electrochemical desorption. In the recombination mechanism, hydrogen atoms are recombined into molecules and simultaneously desorbed. In electrochemical desorption, the hydrogen atoms are removed from the electrode surface according to the reaction. When water is discharged, the electrochemical desorption takes place. In the emission mechanism, adsorbed hydrogen atoms evaporate from the electrode surface as free atoms, which then recombine to form hydrogen molecule.

Iyer and Pickering developed a model assuming a coupled discharge-chemical recombination mechanism for hydrogen evolution and hydrogen entry into the metal. The model enables calculation of the rate constants and hydrogen coverage with the data obtained from hydrogen permeation experiments. A model developed in our group assumes electrochemical recombination mechanism to calculate the kinetic parameters governing hydrogen permeation under corroding conditions.

**Accomplishments:**

Zinc plating has been suggested as a surface treatment technique to mitigate hydrogen permeation through hard alloy. Underpotential deposition of zinc and deposition of
multiple layers of zinc have been beneficial in mitigating hydrogen permeation through steel. Alloying zinc with noble metal like nickel enhances the barrier resistance of electroplates. However small amounts of nickel in the deposit are observed owing to the anomalous nature of the co-deposition. A new Zn-Ni-Cd plating process was developed which offers a unique way of controlling and optimizing the Ni and Cd contents in the final deposits. Using this process a Zn-Ni-Cd ternary alloy with higher nickel content than conventional Zn-Ni bath was synthesized. Apart from Zn-Ni-Cd, two other process namely alkaline Ni-Zn and electroless Ni-Zn-P were developed. Electrochemical techniques were used to characterize the corrosion and hydrogen permeation properties of different coatings in aqueous solutions. These alloys offer maximum corrosion and hydrogen permeation resistance. The experimental results were analyzed using Iyer-Pickering’s model and hydrogen permeation model developed by us at USC. The results of this study can be summarized as follows:

- Zn-Ni-X (X = Cd, P), Non anomalous Ni-Zn and electroless Ni-Zn-P alloys have better corrosion and barrier properties than cadmium and Zn-Ni.
- The polarization and permeation studies indicated that the mechanism for hydrogen evolution reaction on electroless Ni-Zn-P and Zn-Ni-Cd deposits on steel is coupled discharge-recombination with Temkin isotherm for hydrogen coverage. The permeation characteristics of Zn-Ni-X (X = Cd, P) alloys were evaluated under cathodically polarized conditions and were compared with those of Zn-Ni alloy. The adsorption-absorption constant for Zn-Ni-X (X = Cd, P) alloys is one order of magnitude smaller than that of the Zn-Ni alloy, which indicates that the rate at which hydrogen is adsorbed on the surface of the alloy is greatly reduced. It was also found that the recombination rate constant is higher in case of Zn-Ni-P and Zn-Ni-Cd when compared to Zn-Ni. This ensures most of the hydrogen that is adsorbed on the surface to recombine chemically, thus reducing in large extent the hydrogen ingress into the alloy contributing to smaller permeation currents.
- The developed Ni-Zn and and electroless Ni-Zn-P shows excellent corrosion performance in salt fog test conducted as per ASTM B117 standards.

**Summary of Ni-Zn Composites Development**

- **Zn-Ni-Cd** 50/30/20
- **Ni-Zn-P** 74/16/10
- **Ni-Zn** 72/28

- Environmentally benign
- Superior Corrosion Properties
- Superior Mechanical properties
- Ideal Substitutes for Cadmium