Characterization of Hydrogen Permeation for Novel Non-Anomalous Ni-Zn-X (X=P, Cu) Coatings

B. Veeraraghavan, H. Kim, S. P. Kumaraguru, B. S. Haran and B. N. Popov
Department of Chemical Engineering
University of South Carolina
Columbia, SC 29208

Introduction

Hydrogen embrittlement of a metal results in the initiation of micro cracks, which can later lead to the failure of the specimen and is a serious concern in applications of steel. Cadmium is widely used for protection of steel against corrosion. However during Cd deposition, a lot of hydrogen is evolved that permeates into the underlying steel substrates. Apart from this, the toxicity of Cd and its salts makes it necessary to find an alternative coating.[1] Zn-Ni has been projected as the possible replacement of Cd coatings, by virtue of its good corrosion resistance and other engineering properties. We have showed that deposition of thin layers of Zn-Ni or Zn-Ni-Cd alloys reduced the amount of hydrogen permeation into iron up to 90%.[2-3] However, the high Zn content in these alloys (70-90 wt%) limits their corrosion protection. In our earlier work, we have reported the development of non-anomalous Ni-Zn-P alloys using electroless deposition with high Ni content that show promise as a barrier coating for protection of steel.[4] Our current studies have shown that Ni-Zn-Cu alloys also show promise as a possible replacement for Cd coatings.

The objective of this study is to evaluate the corrosion and hydrogen permeation characteristics of Ni-Zn-X (X=P, Cu) coatings as compared to Zn-Ni and Cd coatings. In house developed mathematical model for characterization of hydrogen permeation into metal and alloys under corroding conditions was used to quantitatively estimate various kinetic parameters associated with hydrogen permeation.

Experimental

Low carbon steel (0.1 mm thick) was used as the substrates. Zn, Cd and Zn-Ni deposits were obtained from commercial electrolytes. Ni-Zn-P deposits were developed using an electroless method described previously.[4] Ni-Zn-Cu alloys were deposited cathodically from an alkaline solution containing the sulfate salts of the metals in the presence of complexing agents. Corrosion characterization studies were done in a three-electrode setup using platinum counter electrode and SCE reference electrode. Hydrogen permeation studies were performed in a Devanathan-Stachurski[5] type permeation cell using a cathodic bath of 0.5 M H_3BO_3 + 0.5 M Na_2SO_4 and anodic bath of 0.2 M NaOH. Hydrogen is evolved at the cathodic site of the membrane by applying different negative overpotentials with respect to SCE. The permeation current at the anodic site is continuously monitored by setting the potential at -0.3 V *vs.* Hg/HgO.

Results and Discussion

Figure 1 shows the corrosion rates of the Ni-Zn-P coating as compared with Zn, Zn-Ni and Cd coatings. The plot clearly shows that the corrosion rates of the non-anomalous Ni-Zn-P coatings are five times lower than that of Cd. Several electrochemical techniques reveal the superior corrosion properties of the novel coating when compared with Cd.[4] Similar results have been obtained in the case of electrodeposited Ni-Zn-Cu alloys that will be discussed in detail.

Figure 2 shows the permeation currents for Cd, Zn-Ni and non-anomalous Ni-Zn-P coatings developed in our laboratory. The permeation current densities for Ni-Zn-P alloys were at least one order of magnitude smaller than that of Cd coatings.

Hydrogen Permeation model[2] under corroding conditions was used to compare the permeation characteristics of Ni-Zn-P alloy with other sacrificial coatings like Cd and Zn-Ni. The model assumes a coupled discharge chemical recombination mechanism for hydrogen evolution, which can be presented as follows:

$$M + H^+ + e^- \xrightarrow{k_1} MH_{ads} \qquad [1]$$

$$MH_{ads} + MH_{ads} \xrightarrow{k_2} H_2 + 2M \qquad [2]$$

Hydrogen permeation occurs when part of the hydrogen adsorbed in the first step is absorbed into the metal

$$MH_{ads} \Leftrightarrow MH_{abs} \qquad [3]$$

The hydrogen entry efficiency defined as the ratio of the permeation current density and the cathodic current density is plotted as a function of the overpotential. The results indicated that Ni-Zn-P alloy inhibited completely the hydrogen entry in steel. The observed effects are due to the suppression of the hydrogen absorption by the deposited alloy, and due to the kinetic limitations of the hydrogen discharge reaction. The surface modification resulted in the reduction of the hydrogen absorption rate causing most of the adsorbed hydrogen atoms to form hydrogen molecules rather than to be adsorbed and diffuse into the bulk of the alloy.

Acknowledgments

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References

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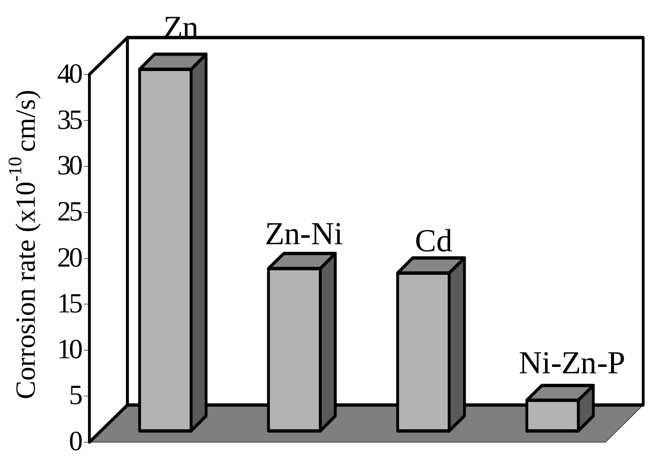

Fig. 1. Comparison of Corrosion Rate of Various Sacrificial Coatings.

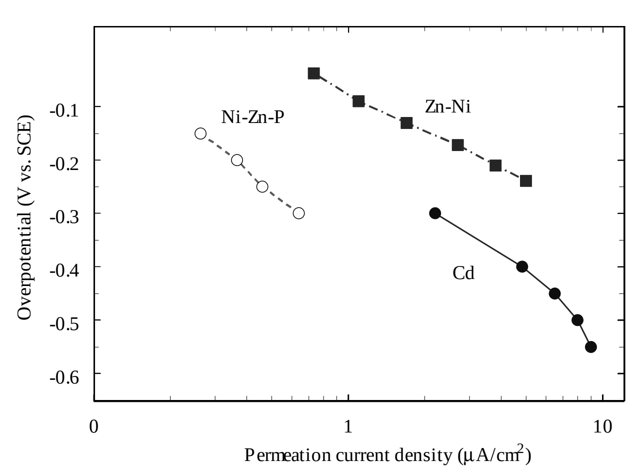

Fig. 2. Permeation current densities for metal composites as a function of applied overpotential.