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Hydrogen permeation inhibition by zinc–nickel alloy plating on steel XC68

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ABSTRACT

The inhibition of hydrogen permeation and barrier effect by zinc–nickel plating was investigated using the Devanathan–Stachurski permeation technique. The hydrogen permeation and hydrogen diffusion for the zinc–nickel (12–15%) plating on steel XC68 is compared with zinc and nickel. Hydrogen permeation and hydrogen diffusion were followed as functions of time at current density applied (cathodic side) and potential permanent (anodic side). The hydrogen permeation inhibition for zinc–nickel is intermediate to that of nickel and zinc. This inhibition was due to nickel-rich layer effects at the Zn–Ni alloy/substrate interface, is shown by GDOES. Zinc–nickel plating inhibited the hydrogen diffusion greater as compared to zinc. This diffusion resistance was due to the barrier effect caused by the nickel which is present at the interface and transformed the hydrogen atomic to Ni_2H compound, as shown by GIXRD.

1. Introduction

Metallic coatings of zinc have been generally used for the protection of mild steel. Zinc–nickel alloy coatings are more attractive because they possess higher corrosion resistance and better mechanical characteristics in comparison with zinc and other zinc alloy coatings [1–8]. Zinc–nickel coatings improve corrosion protection for steels in relatively aggressive environments. It has been found that the maximum protective ability can be reached with the nickel content between 12 and 15 wt.% [9]. Recently, several new technologies for zinc–nickel alloy have been developed [10–15] and further researches for better coating and characteristics are of commercial interests.

There has been renewed interest in studies on hydrogen absorption and hydrogen embrittlement of steel. Metal deposition is usually accompanied by the simultaneous discharge of hydrogen ion or water molecules [16–19]. When hydrogen is liberated on an iron/steel surface during deposition a certain amount of the hydrogen is absorbed by the metal surface and diffuses inside steel. Most probably hydrogen may be liberated to some extent in the atomic state and it is absorbed only in this form. The diffused hydrogen produces some detrimental effects [20] on the mechanical properties of iron/steel, such as reduction in the ductility and loss in mechanical strength leading to hydrogen embrittlement.

Most studies have been concerned with the electroplating process or the corrosion characteristics of the Zn–Ni alloy and have not focused on the hydrogen permeation characteristics of the alloy. However, the hydrogen permeation inhibition is reported by some electrodeposited coatings including Zn–Ni [21].

Researchers have used several metals as surface treatment for the inhibition of hydrogen permeation [22,23]. Surface electroplates may decrease hydrogen permeation by one or more of several mechanisms. The modified surface can act as a physical barrier to hydrogen diffusion due to the low diffusion rate of hydrogen through the electroplate. The discharge kinetics of the hydrogen evolution reaction can be inhibited. Finally, the absorption of hydrogen into the modified surface can be decreased compared to the unmodified surface. More hydrogen will then recombine to form hydrogen molecules which subsequently move away from the surface as hydrogen gas.

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Of the various techniques available for measuring the amount of hydrogen permeated through the mild steel membrane, the technique developed by Devanathan and Stachurski [17] is the simplest and most accurate.

The objective of this study was to investigate the effect of electrodeposition of Zn–Ni alloy on hydrogen permeation inhibition, as compared to plating pure Ni or pure Zn. Thus the hydrogen distribution in the coating was studied by glow discharge optical emission spectroscopy (GDOES) at the interface and within the bulk material. In end, the structure and the diffraction pattern from a very thin layer of zinc–nickel was determined by glancing incidence X-ray diffraction (GIXRD).

2. Experimental

2.1. Electrochemical permeation

In this study, an electrochemical permeation technique was used to study the hydrogen transport in steel and in different coatings.

The materials chosen for this study were disks of rolled steel XC68 (supplied by Lisi Automotive Company with a diameter of 25 mm, a thickness of 1 mm) whose composition is listed in Table 1.

These specimens were ground with Carbimet–SiC grinding paper down to 4000 grit then rinsed with distilled water.

The instrumentation of electrochemical hydrogen permeation was composed of an electrolytic cell with two compartments, each compartment contains a reference electrode (Hg/HgO/NaOH 0.1 M), an auxiliary electrode (wire of Pt), which are relied with a potentiostat/galvanostat (PGP 201 Radiometer) (Fig. 1). Water was circulated in the double jacket in order to maintain a constant temperature in each chamber ($T = 25 \pm 0.5\ ^{\circ}\mathrm{C}$).

The specimen (working electrode) was clamped between the compartments. One side of the specimen acted as the cathodic side, or hydrogen entry side, of the cell. It was galvanostatically polarized at a constant charging current density ($-2\ \mathrm{mA/cm^2}$) in NaOH 0.1 M during 27 h, after polarizing at a cathodic current density of $-20\ \mathrm{mA/cm^2}$ in different solutions (Zn, Zn–Ni and Ni) for 10 min (formation of deposit) and lastly polarizing at a constant charging current density ($-2\ \mathrm{mA/cm^2}$) in NaOH 0.1 M for 36 h.

The compositions of different plating solutions (Zn (alkaline electrolyte: OKLANE/ZINTHIUM by Coventya Company), Zn–Ni (alkaline electrolyte: PERFORMA 280.5 by Coventya Company) and Ni (acid electrolyte: typical Watts nickel bath) are shown in Table 2.

Before starting the permeation experiments in NaOH solutions, the exit side was passivated in desaerated 0.1 M NaOH solution for 12 h under open circuit conditions. After this "chemical passivation", the measured rest potential ($(E_{\mathrm{exit}})_{\mathrm{passiv}} = -240$ mV/Ref) was applied on the exit side for a time sufficiently long (2 h) to get a background current density lower than $+15\ \mathrm{nA\,cm^{-2}}$. In order to avoid the formation of a passive film on the entry side of the sample, argon was introduced in the other (input) empty compartment during this step.

Table 1
Composition of steel XC68 permeation membranes (wt.%).

C	0.69
Si	0.25
Mn	0.75

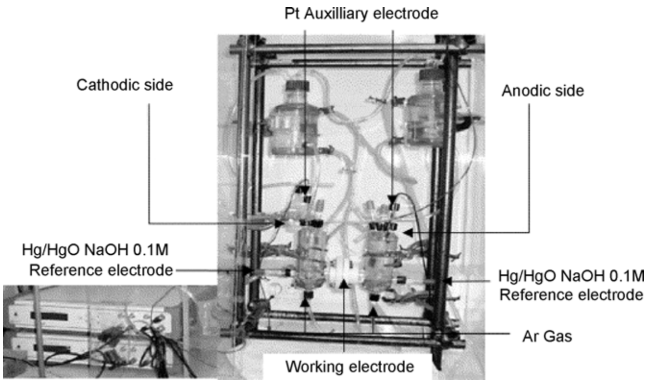

Fig. 1. Apparatus of the permeation cell.

The anodic side, or hydrogen exit side, of the cell was potentiostatically maintained at a constant potential of −240 mV versus reference electrode (Hg/HgO/NaOH 0.1 M) for 63 h and 10 min. This potential (i) to avoid the oxidation of the substrate and (ii) was sufficient to oxidize the hydrogen atoms emerging on the output face according to curve of passivation of steel (Fig. 2).

The anodic current (exit side) gave a direct measurement of the anodic current density J_a detected in this face, J_a is proportional to the hydrogen flow rate (permeation flow).

Solutions on both cells of the membrane were deoxygenated continuously by (Argon U) bubbling.

2.2. Glow discharge optical emission spectroscopy (GDOES)

The distribution of species in the deposit was determined by depth profiling using a Jobin Yvon GD Profiler instrument equipped with a 4 mm diameter anode and operating after optimisation at a pressure of 650 Pa and a power of 30 W in an argon atmosphere.

This low power was retained to decrease the speed of abrasion of the deposits with low thickness and to obtain maximum information at the interface. Quantified compositional results were evaluated automatically utilizing the standard Jobin Yvon quantum Intelligent Quantification software.

The deposits of Zn–Ni are carried out at different current densities ($-10\ \mathrm{mA/cm^2}$ and $-20\ \mathrm{mA/cm^2}$). Electrolysis times are calculated taking into account the faradic efficiencies for each current density in order to have similar thicknesses (approximately 2 μm). The thicknesses of the coating measured by GDOES correlate very well with the ones obtained by X-ray fluorescence.

Table 2
Compositions of different plating solutions.

Zn alkaline electrolyte OKLANE/ZINTHIUM		Zn–Ni alkaline electrolyte PERFORMA 280.5		Ni acid electrolyte Watts nickel bath	
Compound	Concentration	Compound	Concentration	Compound	Concentration
NaOH	$140\ \mathrm{g\,L^{-1}}$	NaOH	$125\ \mathrm{g\,L^{-1}}$	Nickel sulfate	$225\ \mathrm{g\,L^{-1}}$
Base A	$100\ \mathrm{mL\,L^{-1}}$	Base B	$100\ \mathrm{mL\,L^{-1}}$	Nickel chloride	$105\ \mathrm{g\,L^{-1}}$
Oklane solid	$2\ \mathrm{g\,L^{-1}}$	Brightener B	$5.5\ \mathrm{mL\,L^{-1}}$	Boric acid	$45\ \mathrm{g\,L^{-1}}$
Brightener A	$1\ \mathrm{mL\,L^{-1}}$	Ni	$1.2\ \mathrm{g\,L^{-1}}$	–	–
Zn	$14\ \mathrm{g\,L^{-1}}$	Zn	$8\ \mathrm{g\,L^{-1}}$	–	–