

Polyaniline as corrosion protection coatings on cold rolled steel

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A series of electrochemical measurements, including corrosion potential, corrosion current, Tafel's constants and polarization resistance, have been made on polyaniline-coated cold rolled steel specimens under various conditions. Both the base and acid-doped forms of polyaniline were studied. The base form of polyaniline was found to offer good corrosion protection. This phenomenon may not originate merely from the barrier effect of the coatings, because nonconjugated polymers such as polystyrene and epoxy did not show the same electrochemical behaviour.

(Keywords: polyaniline coatings; corrosion; cold rolled steel)

Introduction

Ever since polyaniline was found to have many interesting electrochemical properties and good electronic conductivities upon doping with acids, its potential use in protecting metals from corrosion has been explored. There are a number of reports on the corrosion protection effects of the electroactive polyaniline^{1–8}. In most of cases, polyaniline was employed in the doped form. Wroblewski *et al.*⁶ found that the conductive polyaniline was effective as a corrosion resistant primer with an epoxy topcoat, based on the appearance of the specimen after both laboratory and beach site testing. During the preparation of our present work, Wessling⁷ reported the discovery that proper coating of metals with polyaniline from dispersion (VersiconTM) leads to a significant shift of the corrosion potential in the direction of noble metals and to the formation of a passive metal oxide layer on the surface of the metal. These results are indeed very encouraging. We have been interested in the application of polyaniline as an electroactive material in cathodic protection⁸ and, more recently, as a corrosion inhibiting coating. As the first goal of the present research, we have been attempting to establish the corrosion inhibiting effect of polyaniline by carrying out a series of standard electrochemical measurements on the doped or undoped polyaniline-coated cold rolled steel (CRS) under various conditions. Control experiments were also performed on steel specimens that were either untreated (i.e. unprotected) or protected with conventional polymers (e.g. polystyrene, epoxy resin, etc.) as barrier topcoats.

Experimental

The emeraldine base (EB) of polyaniline was prepared by oxidation of aniline in aqueous 1M HCl with ammonium persulfate as oxidant, followed by treatment

with aqueous ammonia, according to well established procedures^{9–11}. The EB as a fine powder was dissolved in 1-methyl-2-pyrrolidinone (NMP) to give a typically 2 wt% solution. This solution was cast dropwise onto the CRS coupons (1 cm × 1 cm, obtained from Akzo-Nobel Coatings in Columbus, OH, and cleaned thoroughly with water, acetone and ethanol) until the surface was fully and uniformly covered. The EB-coated CRS coupons were dried in air at room temperature for 48 h. The thickness of the EB coating was approximately 14 µm. The Zn²⁺ treatment⁶ was accomplished by immersing the EB-coated CRS in 0.2M Zn(NO₃)₂ solution in THF for ~20 h followed by rinsing with THF and drying in air. To dope the polyaniline, 1M HCl aqueous solution was dropped onto the EB coating followed by drying in air. The colour of the coating changed from dark blue to green upon HCl doping. The CRS coupons were also coated with conventional polymers (e.g. polystyrene, $M_n \sim 8500$ from Fisher) by casting the polymer solution (2 wt%) in THF. Epoxy coatings were made by spreading the mixture of the epoxy resin (Araldite GY2600) with hardener (HY265, both from Ciba-Geigy) uniformly onto the CRS coupons or the polyaniline-coated coupons. The thickness of epoxy coatings was typically about 35 µm.

The coated or uncoated coupons were then mounted to the working electrode so that only the coated side of the coupon was in direct contact with the electrolyte and all the edges were sealed with the epoxy resin. The electrochemical corrosion measurements were performed on an EG&G PAR 273 potentiostat/galvanostat in a standard corrosion test cell equipped with two graphite rod (diameter 6.15 mm) counter electrodes, a saturated calomel reference electrode (SCE) and the gas purge tube, as well as the above mentioned working electrode. The potentials are reported in reference to SCE. All the measurements were made at room temperature. The electrolyte was either HCl (0.1–1M) or NaCl (3.5–5 wt%) aqueous solution.

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Results

The equilibrium open circuit potential of the system was taken as the corrosion potential (E_{corr} in mV versus SCE)^{12–15}. Figure 1 shows plots of the potential against time for the uncoated and polyaniline-coated CRS in 0.1M HCl. The specimens coated with EB or 1M HCl-doped EB have higher corrosion potential values (i.e. more noble) than the uncoated CRS. This is in agreement with previous observations^{6,7}. On the other hand, in non-acidic media such as 3.5 wt% NaCl aqueous solution (Figure 2), the EB-coated CRS had a significantly higher corrosion potential than the CRS coated with 1M HCl-doped EB and the uncoated CRS.

The polarization resistance, R_p (Ω), was measured by sweeping the applied potential from 20 mV below to 20 mV above E_{corr} at a scan rate of 0.2 mV s^{-1} and recording the corresponding current change. The R_p value was obtained as the slope of the potential–current plot^{12–15}. The EB-coated CRS has an R_p value of $3 \times 10^3 \Omega \text{ cm}^{-2}$ in 5 wt% NaCl, which is increased by more than 50% from the uncoated CRS. This increase is more significant for the CRS coated with the $\text{Zn}(\text{NO}_3)_2$ treated EB and epoxy topcoat ($R_p \sim 4 \times 10^5 \Omega \text{ cm}^{-2}$). It should be noted that R_p for the epoxy alone coated CRS was $1 \times 10^4 \Omega \text{ cm}^{-2}$. We have also studied the systems by using a potentiodynamic technique (Tafel plot). The Tafel plots was generated by scanning the potential from E_{corr} to $-250 \text{ mV versus } E_{\text{corr}}$ (cathodic plot) or to $+250 \text{ mV versus } E_{\text{corr}}$ (anodic plot)^{12–15}. Some typical plots recorded in 5 wt% NaCl are shown in Figures 3a and 3b for the uncoated and EB-coated specimen. The corrosion current (i_{corr}) was determined by superimposing a straight line along the linear portion of the cathodic or anodic curve and extrapolating it through E_{corr} , as illustrated in Figure 3a. The slope of the straight line is the cathodic or anodic Tafel's constant (β_c or β_a , respectively). The corrosion current should be inversely proportional to R_p and directly proportional to the corrosion rate (R_{corr} , in thousandths of an inch per year, MPY). The latter can be expressed in the following equation:

$$R_{\text{corr}}(\text{MPY}) = [0.13 i_{\text{corr}}(EW)] / (Ad)$$

where EW is the equivalent weight (g), A is the area (cm^2) and d is the density (g cm^{-3}).

The i_{corr} and R_{corr} values for the uncoated CRS were found to be $\sim 13 \mu\text{A}$ and 6 MPY. These values are significantly lower for the EB-coated CRS ($\sim 3.5 \mu\text{A}$ and 1.7 MPY), and for the CRS coated with the $\text{Zn}(\text{NO}_3)_2$ treated EB and with epoxy topcoat ($\sim 0.1 \mu\text{A}$ and 0.05 MPY). The CRS specimens coated with nonconjugated barrier polymers generally have higher i_{corr} values (e.g. $4.5 \mu\text{A}$ for epoxy and $6.4 \mu\text{A}$ for polystyrene) and therefore greater corrosion rates than the EB-coated CRS. It is noteworthy that upon finishing the electrochemical measurements and exposure to the laboratory environment, the CRS with EB-coatings generally showed less or no corrosion on the uncoated surface or beneath the EB coating, while the other specimen had visible rust formation¹⁶.

Conclusion

In summary, we have performed a series of electrochemical corrosion measurements on polyaniline-coated CRS specimens under various conditions. Both

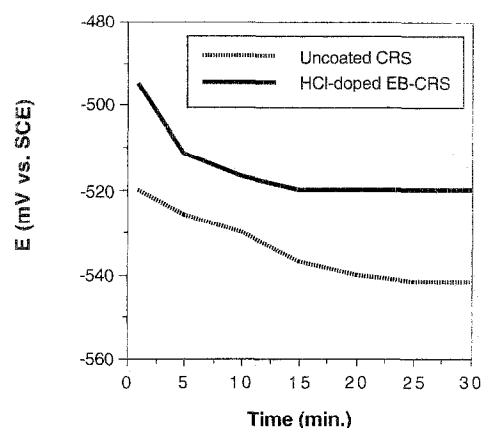


Figure 1 Plot of open circuit potential in 0.1M HCl versus time

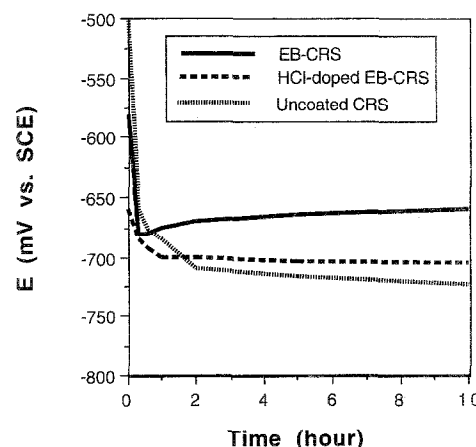


Figure 2 Plots of open circuit potential in aqueous 3.5 wt% NaCl versus time

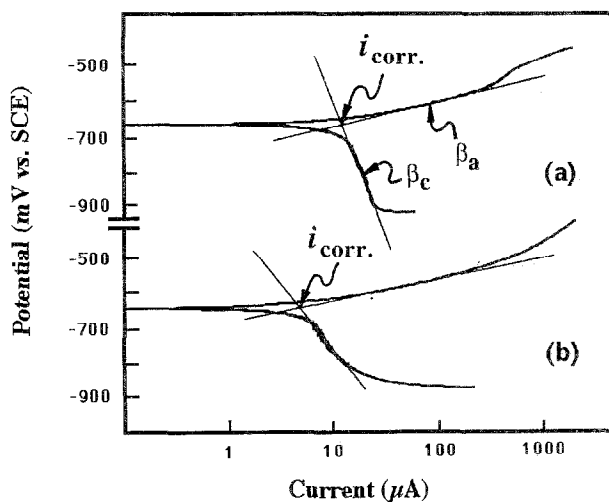


Figure 3 Tafel plots for (a) uncoated CRS and (b) EB-coated CRS measured in 5 wt% NaCl aqueous solution

the base and acid-doped forms of polyaniline were studied. The base form of polyaniline was found to offer good corrosion protection in the aqueous NaCl medium, as evidenced by the increase in the corrosion potential and polarization resistance, and by the decrease in the corrosion current in comparison with the uncoated CRS. This phenomenon may not originate merely from the barrier effect of the coatings

because the nonconjugated polymers, such as polystyrene and epoxy, did not show the same electrochemical behaviour. The polyaniline base with zinc nitrate treatment plus epoxy topcoat appeared to give better overall protection relative to other coating systems in this study, which is consistent with the observation reported by Wroblewski *et al.*⁶. Further investigation is in progress in our laboratory to gain a better understanding of these interesting, but very complex, corrosion protection systems.

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