JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 18, Preprint 35 submitted 9 July 2015

Appraisal of Sacrificial Anode Malperformance Due to Polarity Reversal of Galvanic Coupling between Mild Steel and Zinc in Hot Sodium Bicarbonate ($NaHCO_3$) Solution

Syed Asad Ali Zaidi[1], Azhar Mahmood*[1], Ashraf Ali[2]
[1]*PNEC, National University of Sciences & Technology, Pakistan.* drazhar@pnec.nust.edu.pk
[2]*Department of Materials Engineering, NED University of Engineering & Technology, Pakistan.*

Abstract

Electrochemical behavior of mild steel and zinc coupling has been examined in 0.01M sodium bicarbonate ($NaHCO_3$) solution at 65°C. Passivation occurred upon mild steel and zinc together in this condition. Their potentiodynamic graphs have revealed that mild steel passivated more slowly rather than zinc. This furnished the surveillance of a transitory condition of polarity reversal in the mild steel-zinc galvanic couple. In order to prove these results, a set of galvanically coupled mild steel and zinc electrodes have been placed in 0.01 M sodium bicarbonate solution to analyze their behavior at room temperature (25°C) and at higher temperature (65°C).

A temporary polarity reversal phenomenon has been evidenced in 0.01 M sodium bicarbonate solution at higher temperature where zinc function shifted to cathode because of the formation of thick layer of corrosion products making it passive much earlier rather than mild steel which protect zinc from further corrosion whereas mild steel altered to anodic behavior hence undergo corrosive attack. These results were helpful to understand malperformance of sacrificial zinc anode in sub tropical/tropical marine environment having ample amount of bicarbonate ions in warm waters.

Keywords: Corrosion, polarity reversal, potentiodynamic polarization.

Introduction

Mild steel is a chief fabrication material for the majority of engineering structures owning to its useful specific properties including good malleability, ductilability, weldability, medium tensile strength, and its easier to cold-form so making it facile to handle during structural fabrications [1, 2]. But on other hand it is more vulnerable to corrosion due to its poor passivation as its oxide layer formed by corrosion does not have good adhesion to under

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laying metal and peel off readily causing exposure of fresh metal surface hence corrosion continue without obstruction. Extensive corrosion ultimately results structural weakness and disintegration of the metal [3-4]. Therefore, various techniques like impressed current cathodic protection methods, sacrificial anode, galvanized coatings and barrier film coatings etc. are in used to protect mild steel structure against corrosion. Marine mild steel structures are usually protected by sacrificial anode techniques, involving integration of zinc auxiliary anode [5]. Under standard ambient conditions, zinc has lower reduction potential (-763 mV vs. SHE) than mild steel (-440 mV vs. SHE) therefore zinc function as anode versus iron thus protecting mild steel structures. However, zinc potential may vary depending alloy composition, presence of anions in environment and water pressure. Therefore, polarization of the mild steel-zinc couple could be inverted in an aerated electrolyte above 60^{o}C temperature, with the zinc becoming cathodic to the mild steel. This phenomenon called polarity reversal, which resulted from the ennoblement of zinc [6, 7]. A thin electrically non-conductive zinc oxide layer caused cathodic depolarization while anodic spot at gapes in this layer may be clogged by the deposition of zinc carbonate precipitates which induced passivity on zinc anode making it redundant. Therefore zinc will no longer cathodically protect the mild steel due to polarity reversal. This is also reported in literature that polarity reversal may not only lack preservation but also promote the corrosion of a structure above that of an unprotected structure [8, 9]. Marine environment provides plenty of moisture for ionic conduction hence promote electrochemical corrosion. Marine water has various corrosive salt species like Cl^-, HCO_3^- etc. which promotes polarity reversal thus reduced anode efficiency which restrict the choice of zinc anodes to ambient temperature marine applications [10, 11]. The aim of subject study was to evaluate the malfunctioning of zinc sacrificial anode due to polarity reversal phenomenon of zinc and mild steel coupling at higher temperature (at 65^{o}C).

Experimental

Electrode Preparation for Potentiodynamic Polarization Measurements

HR-235 Carbon steel was opted for working electrode fabrication. Its composition was ascertained by using X-ray Fluorescence Spectroscopy (INNNOVEX SYSTEMS) and was found to be 0.07 % Cu, 0.36 % Mn and 99 % Fe. The composition of zinc electrode material was established by the same procedure and found to be 99.97 % Zn. The electrodes of surface area 1×1 cm^2, were prepared by mounting the metal in epoxy and drying the samples for one day. These samples were then grinded using series of grinding papers (180, 220, 320, and 400) on MoPao 260 E Grinder machine. Subsequently samples were polished using

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ISSN 1466-8858 Volume 18, Preprint 35 submitted 9 July 2015

BENETEC polishing machine to remove all kinds of grinding marks and were then rinsed with water (Figure 1).

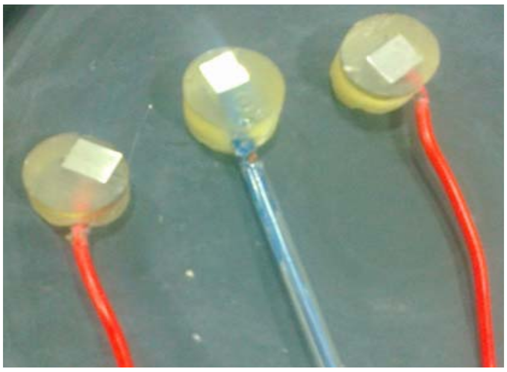

Figure 1: Mild steel (outer side) and Zinc (center) electrodes.

Electrochemical Apparatus

An electrochemical cell was prepared by customizing Gamry Instruments MultiPort™ Cell Kit while employing above fabricated electrodes. Fresh 0.01 M sodium bicarbonate ($NaHCO_3$) solution was prepared in water and served as an electrolyte. Experiments were designed to carry out potentiodynamic polarization scans of subject electrochemical cell by using a Gamry G 750 Potentiostat. The potentiodynamic graphs were recorded at 5 mV/min scan rate. Electrochemical cell was covered with a heating mantle connected to Omega Bench top Controller CSi8D series to maintained temperature of the cell at 65 ^{o}C ± 0.5 (Figure 2).

Figure 2: Experimental setup of electrochemical apparatus

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Coupling of Zinc and Mild Steel Electrodes

Mild steel and zinc electrodes were electrically connected and allowed to corrode freely in freshly prepared 0.01 M Sodium Bicarbonate ($NaHCO_3$) solution. Electrochemical behavior of mild steel and zinc coupling has been analyzed at room temperature (25 °C) and at higher temperature (65°C). Subsequently extent of corrosion at these working electrodes was ascertained by taking stereo micrographs of corroded surfaces of electrode.

Results and Discussion

Above mentioned experiment has furnished potentiodynamic scanning curve for mild steel and zinc electrodes at 25°C and at 65°C in 0.01 M sodium bicarbonate ($NaHCO_3$) solution. These results were analyzed to conclude their passivation behavior. Moreover, stereo micrographs of mild steel and zinc electrodes after coupling have been proved helpful to establish polarity reversal behavior during coupling.

Corrosion Behavior of Mild Steel and Zinc Coupling at Room Temperature (25 °C)

The corrosion behavior of mild steel and zinc couple has been analyzed at room temperature (25 °C) in 0.01 M sodium bicarbonate ($NaHCO_3$) solution. The electrodes were connected and allowed to corrode freely in the solution. After 02 hours, electrodes were retrieved and their surfaces were scanned via stereo microscope.

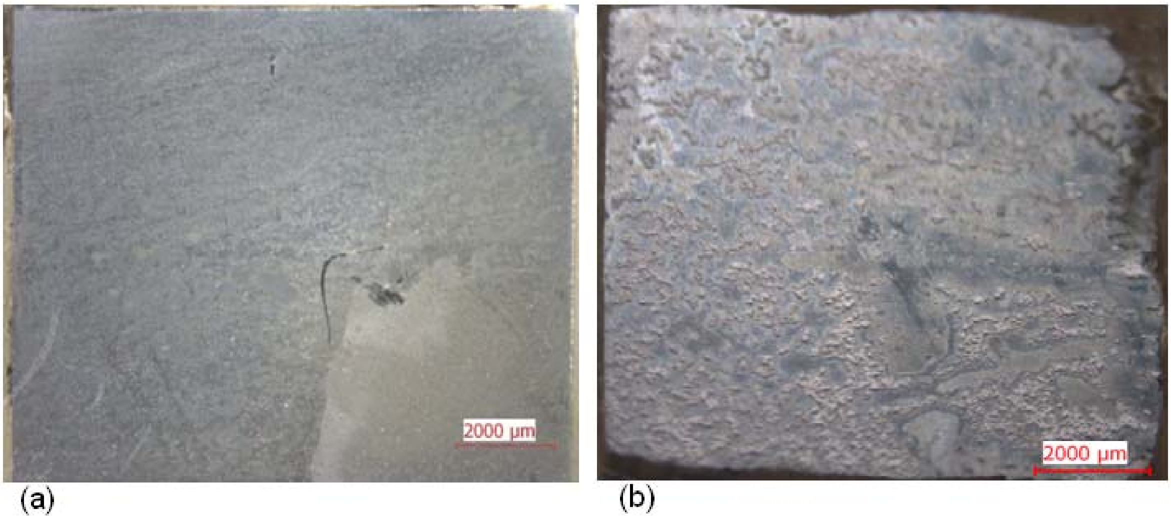

Figure 3: Stereo micrograph of (a) mild steel and (b) zinc after galvanic coupling at room temperature (25 °C).

Comparison of these stereographs have confirmed active galvanic coupling between mild steel and zinc electrodes. Stereo micro image of mild steel depicted clear unreacted/protected surface which intended cathodic polarity on mild steel during coupling (Figure 3a). However, stereo micrograph of zinc electrode has shown corroded/reacted topography which established its role as sacrificial anode during subject coupling (Figure 3b). These observations have complete coincidence with sacrificial anode behavior of zinc electrode via galvanic coupling while have contradiction with polarity reversal phenomena. It is therefore, concluded that mild steel and zinc coupling at room temperature (25 °C) in 0.01 M Sodium Bicarbonate solution have active sacrificial anode coupling behavior while its lack any polarity reversal phenomenon.

Corrosion Behavior of Mild Steel and Zinc Coupling at Higher Temperature (65 °C)

The corrosion behavior of mild steel and zinc coupling has been analyzed at 65°C temperature in 0.01 M sodium bicarbonate ($NaHCO_3$) solution. These electrodes were connected and allowed to corrode freely under above mentioned conditions. After 02 hours, electrodes were retrieved and their surfaces were scanned via stereo microscope.

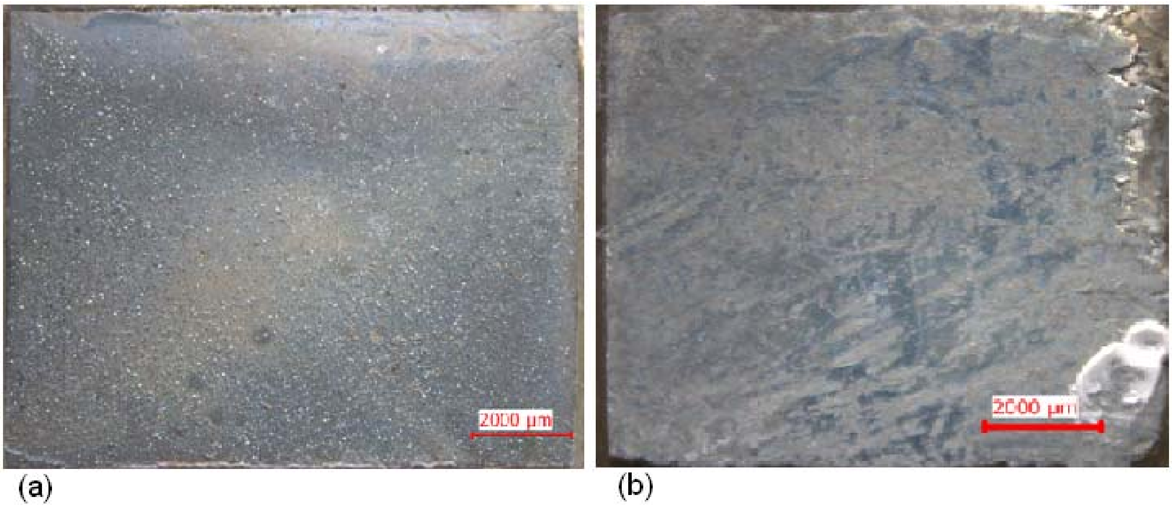

Figure 4: Stereo micrograph of (a) mild steel and (b) zinc after galvanic coupling at higher temperature (65 °C).

Comparison of these stereo micrographs has confirmed absence of sacrificial zinc anode galvanic coupling between mild steel and zinc electrodes in these conditions. Micrograph of mild steel electrode showed corroded faces which evident that mild steel has no more protected by cathodic polarity, induced formerly by sacrificial zinc anode (Figure 4a). On other hand, Stereo-image of zinc electrode has displayed development of an intact passive layer on surface which inhibited anodic polarity of zinc by its passivation (Figure 4b). Contradict to this, whole nature of polarity and intended role of mild steel and zinc electrodes in previous sacrificial zinc anode galvanic coupling has been inverted. Now passivated zinc has been behaved as cathode and been protected while mild steel has been behaved as anode and been corroded. This phenomenon is called polarity reversal. This has indicated that under subject conditions, zinc is passivated much faster than mild steel which later on confirmed by comparison of Potentiodynamic curves of zinc and mild steel. These curves have pointed out that zinc passivation occurs in short time interval as compared to mild steel.

Potentiodynamic Curve for Mild Steel and Zinc at 65 °C

The potentiodynamic curve has been plotted for mild steel and zinc in 0.01 M sodium bicarbonate ($NaHCO_3$) solution at 65°C by Computerized Potentiostat at a scan rate of 5mV/min.

Figure 5 has exhibited the cathodic and anodic potentiodynamic curves for mild steel electrode. In cathodic branch mild steel showed a sluggish initial rise in potential with decrease of current density caused by slowing down reduction reaction at mild steel cathode. Subsequently it stabilized at potential closer to -640 mV due to its passivation. A patchy corrosive attack was noticed on the mild steel after retrieving from solution. A thick translucent corrosion product film was found on some areas of mild steel surface.

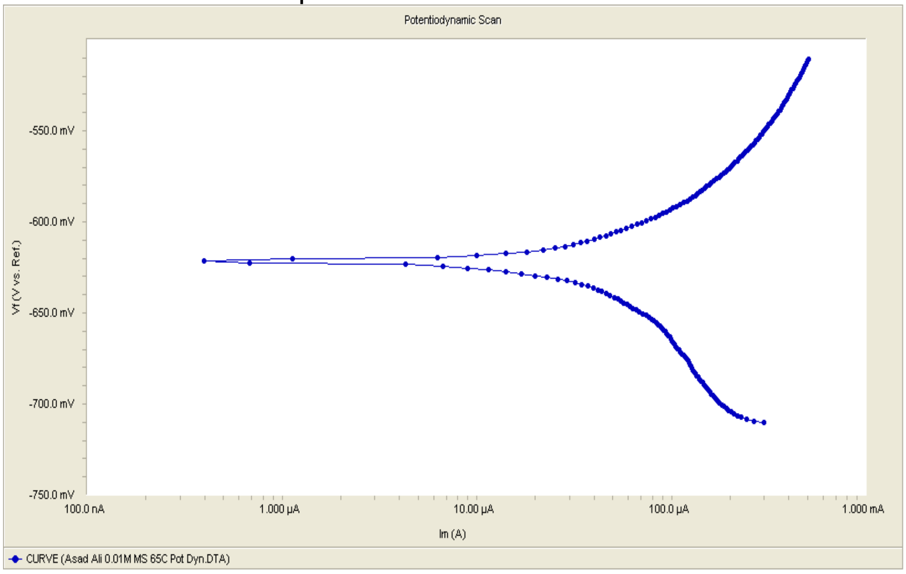

Figure 5: Potentiodynamic curve for mild steel at 65°C

JCSE The Journal of Corrosion Science and Engineering
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Figure 6 has depicted the cathodic and anodic potentiodynamic curves for zinc electrode. In cathodic branch zinc showed a rapid initial rise in potential with decrease of current density i.e. with deceleration of reduction reaction at zinc cathode. Subsequently it stabilized at potential closer to -960 mV due to zinc passivation. This is further confirmed by presence of a very thin, transparent / white passivation product film found on zinc electrode after retrieval from the solution.

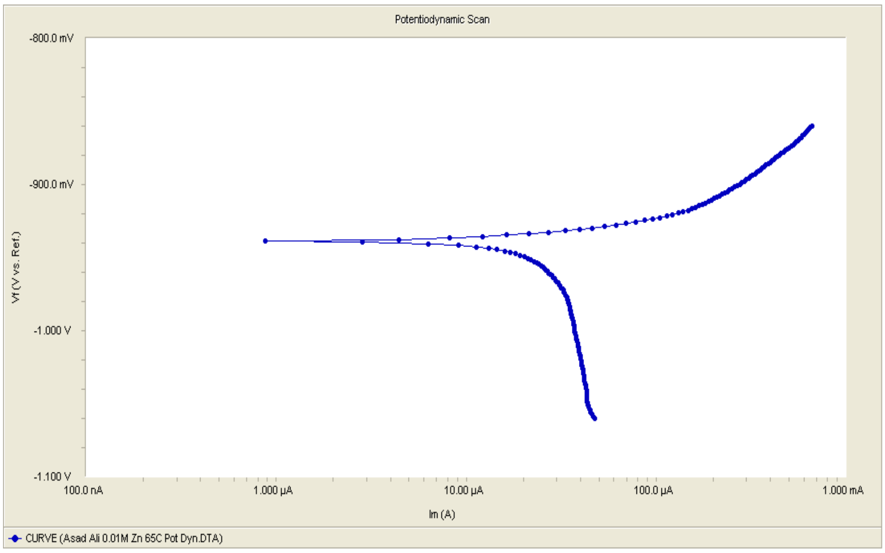

Figure 6: Potentiodynamic curve for zinc at 65°C

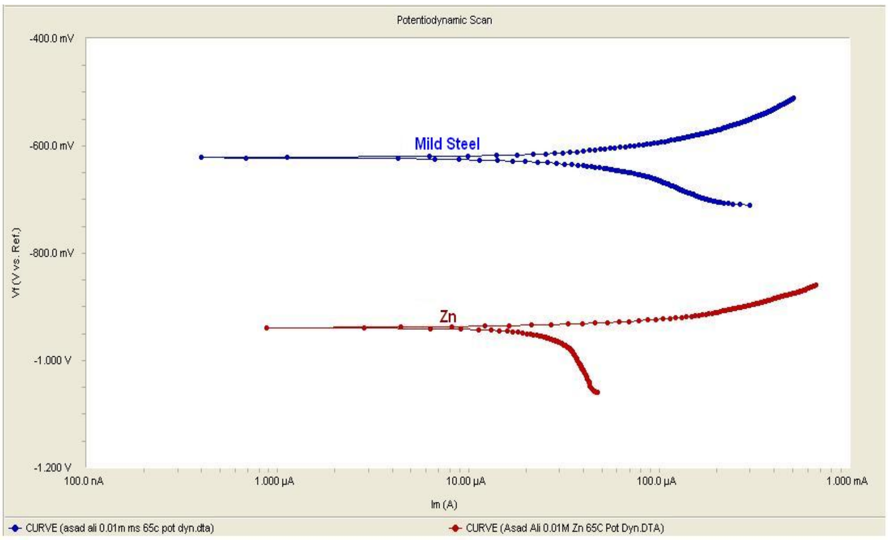

Figure 7: Comparison of potentiodynamic curves for zinc and mild steel

Abovementioned potentiodynamic curves for mild steel and zinc has been compared in Figure 7. Comparison of both potentiodynamic curves has revealed that although like zinc, mild steel also passivated after a adequate exposure to subject conditions but zinc corrosion reaction was more polarizable than the steel corrosion reaction as a result zinc passivated earlier causing reversal of polarity.

Conclusion

A transitory phenomenon of polarity reversal has been evident in the zinc-mild steel galvanic coupling when exposed to the hot sodium bicarbonate ($NaHCO_3$) solution. This is because of relatively more rapid passivation of zinc as compared to mild steel in these conditions as exhibited in their potentiodynamic graphs.

Marine water has ample amount of bicarbonate ions therefore these conditions for polarity reversal are frequently achieved in sub-tropical/tropical marine environment causing malperformance of sacrificial zinc anode. Major disadvantage resulted from polarity reversal is the malfunctioning of zinc so did not cathodically protect the steel structures.

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