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Galvanic corrosion of carbon steel coupled to antimony

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ABSTRACT

Galvanic corrosion of carbon steel coupled to antimony was studied in aerated and N_2-purged electrolytes at ambient and 60 °C temperatures. Free corrosion potential of antimony and carbon steel shifts to more active values with increasing temperature and N_2 purging of the electrolyte. Under all experimental conditions, antimony remains less electronegative than carbon steels. Aeration and temperature affect potentiodynamic behaviour of both materials. As a consequence, the corrosion current for the antimony–carbon steel couple increases with increasing temperature and with aeration. There was a good agreement between the corrosion currents obtained through the Evans' experiment and super-imposed potentiodynamic scans.

1. Introduction

Antimony has many uses. For example, it is used in the semiconductor industry in manufacturing electronic devices through electrodeposition [1,2], or it is used in pH-indicator electrodes [3]. A number of publications describe the electrochemistry of antimony [4–9] with respect to its use as an alloying additive in lead alloys for casting lead-acid battery grid components [10]. Little work, however, has been reported on antimony in corrosion related studies.

In general, antimony exhibits stability [11,12] in the atmosphere and high resistance to sulphuric, nitric and hydrochloric acids at ambient temperature, and general resistance to various environments wherein the antimony trioxide, Sb_2O_3, is sparingly soluble. In the middle of 20th century, these attributes prompted development of antimony plating technology [13–15]. However, the technology never reached a commercial success predominantly due to the inherent brittleness of antimony and its low tensile strength. Le et al. [16] reported that addition of 0.1% of antimony to low-alloy steel markedly improved corrosion behaviour, which was ascribed to the formation of an oxide film, *i.e.* Sb_2O_5, on the steel surface. On the other hand, Golubev et al. [17] reported localised corrosion of carbon steel in an industrial setting in association with the process related deposition of non-continuous (defective) layers of metallic antimony. The process of antimony deposition has been referred to as *cementation* [18,19], and in general it is the reduction of antimonyl ions, SbO^+, which occurs in association with oxidation of iron. The process can be described by the following electrochemical reactions:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(oxidation)} \tag{1}$$

and

$$SbO^+ + 2H^+ + 3e^- \rightarrow Sb_{(s)} + H_2O \text{ (reduction)} \tag{2}$$

Similar process may also occur in other industrial settings, where presence of antimony in the ionic form is intrinsic to process media, for instance geothermal fluids [20,21].

In the current work, we have studied electrochemical behaviour of a conventional carbon steel and antimony in a chloride containing environment, with the focus to establish severity of the localised corrosion when such materials are coupled together. The preliminary results cover the effect of temperature and the level of solution aeration on the corrosion current density. The on-going work will expand on the effects of higher temperature, *i.e.* >60 °C, solution pH and its composition with regards to concentration of chloride and ferric ions, presence of low level H_2S, and the effect of cathodic–anodic area ratio. It will also include potential-pH equilibrium diagrams for the relevant systems and environmental conditions.

2. Experimental

2.1. Electrode preparation

High purity (99.999%) antimony (Goodfellow Materials, England) and conventional carbon steel (AISI 1018), both in the form of rods with 6 mm diameter were used as experimental materials in as received condition. Electrodes were prepared from approximately 20 mm long pieces, which were cut from the supplied materials. One end of each specimen was then soldered to a copper lead to provide electrical connection, degreased with ethanol and finished by rinsing using acetone. Such prepared specimens were

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then mounted in K36 coating and laminating epoxy resin (Nuplex Industries Ltd., New Zealand). Attention was paid to avoid introducing bubbles at the metal-resin interface, as these would interfere with experiments; prepared electrodes that contained such bubbles were discarded. Electrodes were then stored in a desiccator and prior to each measurement the surfaces ground using 1000 grid emery paper and rinsed with distilled water.

2.2. Electrochemical measurements

All electrochemical measurements were obtained by using a model PGZ 100 potentiostat (Radiometer Analytical) connected to a personal computer via an RS-232 interface and controlled through the VoltaMaster 4 electrochemical software (Radiometer Analytical). A calomel electrode with saturated KCl (SCE) was used as the reference (all potentials reported were referred to SCE) and a platinum electrode as the auxiliary. Measurements were conducted using a typical three-electrode electrochemical cell with a double-wall arrangement. Such a custom-made design allowed for a hydronic heating of the experimental electrolyte, with both the heating mantle (Electrothermal, UK) and the peristaltic pump (Watson-Marlow 505S, UK) located outside the Faraday cage to minimize electromagnetic interference.

The experimental electrolyte was prepared using distilled water and analytical grades of sodium and potassium chlorides (Scharlau Chemie S.A., Spain) at the ratio of 3.7, with the total concentration of chloride ions of 1000 mg dm^{-3}. The pH of the electrolyte was adjusted to 5.4 using 0.05 mol dm^{-3} solution of sulphuric acid. In the case of measurements conducted in deaerated electrolytes, high purity nitrogen gas was used for purging for 1 h before starting a measurement and for shielding atmosphere in the cell during the measurements.

Potentiodynamic scans for both materials were conducted after a 900 s hold at the free corrosion potential, E_{corr}, and then initiated from the adopted E_{corr} in either anodic or cathodic direction at a scan rate of 0.1 mV s^{-1}.

The corrosion current that was expected to take place at the mixed potential of antimony–carbon steel couple was measured using the Evans' experiment, where the more electronegative material (carbon steel) was used as the working electrode and the less electronegative material (antimony) was the auxiliary electrode. The galvanostatic steps, 0.1–0.2 μA, were then applied to such an arrangement and individual potentials of both electrodes measured against the SCE using the following condition: d(WORK)/dt and d(AUX)/dt < 3 mV min^{-1} or Maximal-Step-Duration equals 30 s. Experiments were repeated three times for each experimental condition and the corrosion current, I_{corr}, for each measurement established as the intersection of corresponding potential *vs.* current curves.

3. Results and discussion

3.1. Free corrosion potential

Figs. 1 and 2 show respective records of E_{corr} for uncoupled antimony and carbon steel electrodes exposed to the aerated and N_2-purged electrolyte at ambient temperature, *i.e.* 20 °C, and at temperature of 60 °C. E_{corr} of antimony remained constant throughout the entire period of monitoring under all experimental conditions. Similar behaviour was also observed for carbon steel exposed to the N_2-purged electrolyte at both temperatures. Under aerated conditions E_{corr} of carbon steel showed a decaying trend, which became more pronounced with increasing temperature. In general, such a behaviour, *i.e.* decaying trend, is typical for formation of porous hydroxide layers, which slow the rate of metal dissolution, but do not protect it from further dissolution [22].

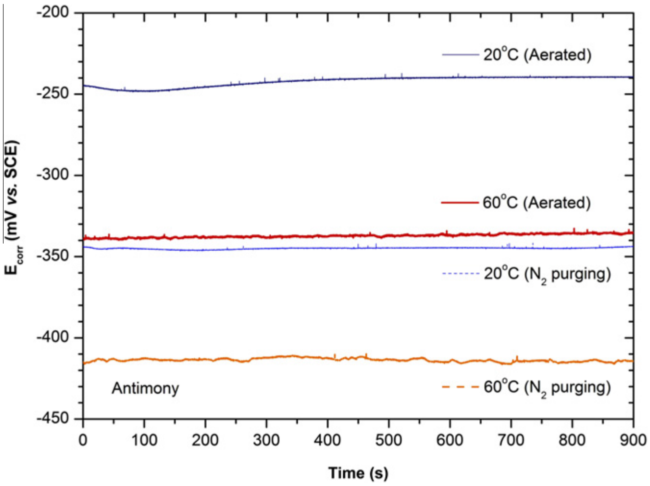

Fig. 1. Records for the free corrosion potential, E_{corr}, of antimony in the aerated and N_2-purged electrolyte at 20 and 60 °C.

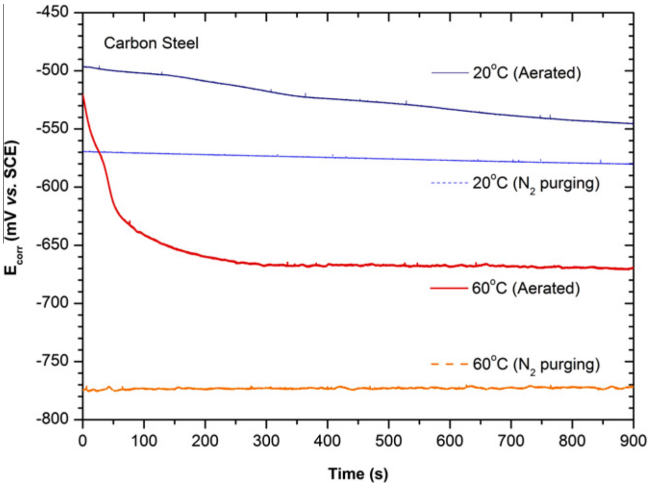

Fig. 2. Records for the free corrosion potential, E_{corr}, of carbon steel in the aerated and N_2-purged electrolyte at 20 and 60 °C.

The values of E_{corr}, recorded after 900 s of monitoring, were plotted as a function of temperature in Fig. 3, which shows that antimony remains less electronegative material (cathodic) than carbon steel under all experimental conditions. E_{corr} of antimony and carbon steel shift to more active values with both increasing temperature and N_2 purging. This observation is not surprising since the E_{corr} in the N_2-purged environment would be controlled by the H–H^+ half-cell reaction, which is on the active side of the standard half-cell potentials scale, when compared to the O_2–OH^- half-cell reaction that would dictate E_{corr} in aerated environment. Experimentally, such a shift in E_{corr} due to level of solution aeration was reported for instance for AISI Type 304 stainless steel [23] and high purity aluminium [24]. The effect of temperature is also related to the concentration of oxygen in the electrolyte, since its concentration in aqueous solutions generally decreases with increasing temperature; for instance it falls from 14.2 mg dm^{-3} at 1 °C to 6.4 mg dm^{-3} at 40 °C in water [25]. Consequently, diffusion limited current associated with the oxygen reduction reaction decreases with decreasing oxygen concentration, which results in less-efficient consumption of electrons and a negative shift in E_{corr}.