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Electrochemical and SVET Studies on the Typical Polarity Reversal of Cu–304 Stainless Steel Galvanic Couple in Cl⁻-Containing Solution with Different pH

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ABSTRACT

The typical polarity reversal of the Cu–304 stainless steel galvanic couple (Cu–304SS GC) in Cl⁻-containing solution with different pH was investigated by open circuit potential (OCP), potentiodynamic polarization, and galvanic current techniques in conjunction with scanning vibrating electrode technique (SVET) and scanning electron microscopy (SEM). The results showed that the change in pH of the solution has a significant effect on the corrosion behavior of 304SS. The typical polarity reversal occurs in Cu–304SS GC in Cl⁻ solution with pH 0, in which the red copper is cathodic to 304SS, while in the solution with pH 6, 4, and 2 the red copper is anodic to 304SS. With the decrease in pH, the 304SS changes from the passive state to the activation state due to the dissolution of the passive film on the surface thereby facilitating the polarity reversal of the Cu–304SS GC.

1. Introduction

Galvanic corrosion is a common type of corrosion that exists widely in the shipping, oil and gas, aviation, and construction industries and medical equipment. It normally leads to corrosion failure in heat exchangers, ship propellers, valves, condensers and medical implants [1–9]. There exist extensive studies on the influence of different environmental variables on the galvanic corrosion, such as the ratio of cathode area to anode area [5,10], the distance between electric dipoles [11,12], the temperature of the electrolyte [13,14], and so on. Studies have demonstrated that the effect of the ratio of cathode area to anode area on the galvanic corrosion depends on whether the corrosion is under anodic or cathodic control [15,16]. With regard to the effect of temperature on galvanic corrosion, it was found that the galvanic corrosion current increases with increasing temperature due to the accelerated kinetics caused by the thermally activated process at elevated temperature [6,13,14]. The influences of other factors, such as the potential and the polarization characteristics of the

materials [17], the dissolved oxygen content [18,19], the flow velocity of the medium [10,20,21], and pH [22], on the galvanic corrosion have also been thoroughly investigated.

Nevertheless, there are still some aspects that have not been studied in depth. In fact, various factors such as temperature, pH, and the change in the ratio of cathode area to anode area would result in a suddenly accelerated corrosion process on the cathode or anode, which becomes corroded seriously on the galvanic couple therefore a potential hazard. Polarity reversal is a phenomenon that occurs in some galvanic couples, which was first reported by Schikorr on a zinc/steel couple in hot supply water in which iron became anodic to zinc, causing a serious problem for the galvanized steel hot water tanker [23]. The most studies on polarity reversal have been focused on the effect of solution concentration [24,25], solution composition [24,26], and the temperature [27,28] of the solution on polarity reversal. However, the effect of pH on polarity reversal is almost unknown and further understanding of polarity reversal is needed. Fraunhofer et al. [24] investigated the polarity reversal of a zinc/mild steel couple and found that the polarity reversal of the couple occurred in 0.05 M NaHCO₃ solution at elevated temperatures due to the passivation of zinc. Glass et al. [27] studied the galvanic corrosion of a zinc/steel couple exposed to hot oxygen-saturated sodium bicarbonate solution. The results indicated that a temporary condition of

polarity reversal took place due to the more rapid passivation of zinc in such an environment, and it did not persist after the steel passivated.

The polarity reversal of the galvanic couple is commonly studied through the conventional electrochemical techniques, such as galvanic current [23,24], open circuit potential (OCP) [25], and polarization curves [25,27]. The experimental results from these conventional electrochemical techniques reflect average values over a relatively large surface area of the materials. However, it is well known that corrosion is often localized, for which the utilization of local electrochemical analysis is necessary. In order to investigate the underlying mechanism of the polarity reversal of Cu–304 stainless steel galvanic couple (Cu–304SS GC) as a function of pH, scanning vibrating electrode technique (SVET) was used, which is specially designed to investigate the local anodic and cathodic activities on the surface of the electrodes and then to determine the corrosion type [9].

The Cu–304SS GC is commonly found in equipment used in petroleum, chemical, pharmaceutical and energy industries. In some cases, the service environment of such equipment (i.e. reactor and heat exchanger) can change from near neutral to a strong acid condition in a short period of time, leading to serious security risks due to the failure of cathodic protection caused by the typical polarity reversal. Therefore, an in-depth study with respect to the mechanism of the polarity reversal of Cu–304SS GC is of great importance. This work was considered essential on the basis of that Cu–304SS GC is very common in various industries, but that there is rare information regarding the influence of pH on the polarity reversal of Cu–304SS galvanic corrosion in solution containing Cl^-.

This study was focused to elucidate the influence of pH on the polarity reversal of the Cu–304SS GC in solution containing Cl^-. The OCP, potentiodynamic polarization, galvanic current, SVET and immersion tests were used to investigate the typical polarity reversal of Cu–304SS GC in Cl^-- containing solution as a function of pH. The surface morphologies were evaluated by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and electrolyte preparation

The materials used in the electrochemical testing were red copper (99.99 wt%) and 304SS plates. The chemical composition of the tested 304SS is listed in Table 1. The samples with dimensions of $3 \times 5 \times 10\ mm^3$ were mounted in epoxy resin with an exposure area of $0.15\ cm^2$ for the single electrode. For the galvanic couple electrode, the Cu–304SS couple with a PVC membrane in between

Table 1
Chemical composition (in mass%) of the 304 stainless steel used in this work.

Elements	Cr	Ni	C	Si	P	S	Mn	Fe
Content	18.4	8.1	0.06	0.47	0.02	0.011	0.81	Bal.

was mounted in epoxy resin with an exposure area of $0.3\ cm^2$. Each electrode was welded to copper wires to ensure an electric connection for electrochemical measurements (as illustrated in Fig. 1a). The materials used for the SVET tests were red copper (99.99 wt%) and 304SS wires with 1.2 mm in diameter. The two electrodes were embedded in the epoxy resin with a gap of approximately 1 mm (as shown in Fig. 1b). The rear of the wires was connected by Sn welding to provide an electrical contact.

The samples were ground progressively down to 2000 grits finish by using waterproof silicon carbide (SiC) paper. Sample surfaces were degreased with acetone then cleaned by double-distilled water prior to immersion in the experimental solutions.

The electrolyte used for the tests was 1 M sodium chloride (NaCl) prepared by double-distilled water, and the initial pH of the electrolyte was adjusted to 6, 4, and 2 separately for use by using 1 M hydrochloric acid (HCl) solution. The 1 M NaCl aqueous solution with pH 0 was replaced by 1 M HCl solution, since equal concentrations of Cl^- ions have acquired.

2.2. Electrochemical tests

Electrochemical tests were performed using a conventional three-electrode cell including a saturated calomel electrode (SCE) reference electrode and a Pt counter electrode. A Gamry Interface-1000 electrochemical station was employed to carry out the electrochemical tests. Prior to each potentiodynamic polarization scan, the specimens were conditioned in 1 M Cl^- solution with different pH for 24 h to reach a stable OCP. The potentiodynamic tests were carried out at a scan rate of 0.1667 mV/s with a range of −0.8 to +1.2 V versus OCP. All electrochemical tests were conducted at room temperature (25 ± 1 °C) in the naturally aerated solutions. The electrochemical tests were conducted in triplicate in order to ensure the reproducibility of the data.

2.3. Immersion tests and characterization

The immersion tests were performed in a 250 mL beaker for 48 h at 25 °C. The galvanic couple specimens and solutions with different pH used in the immersion tests were identical to those described in Section 2.1. After the immersion tests, the samples were rinsed with distilled water and ethanol, and then dried in a

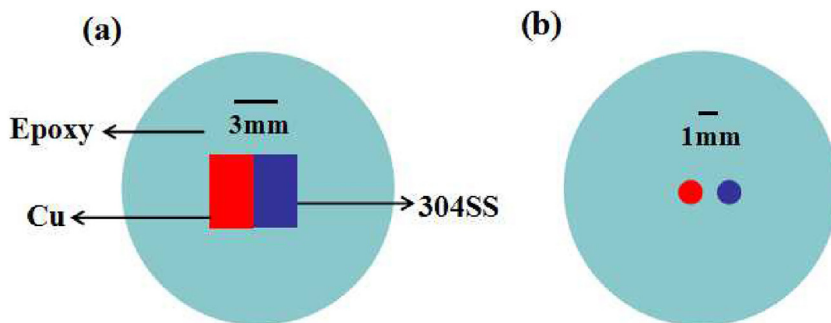**Fig. 1.** Schematics of top views of the galvanic couple electrode samples in an epoxy resin: (a) electrochemical test and (b) SVET test.