



ORIGINAL ARTICLE

Marine bio-fouling of different alloys exposed to continuous flowing fresh seawater by electrochemical impedance spectroscopy



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Abstract The petroleum industry and desalination plants suffer from marine bio-fouling problems that have a major role in the stimulation of the corrosion process. Thus, the aim of this study was to investigate the effect of the micro and the macro-organisms, on the corrosion behavior of different alloys used in Kuwait's industries. The alloys used in this study were; sanicro 28, stainless steel 316L, Cu–Ni 70–30, and titanium. The electrochemical impedance spectroscopy was used in this study in order to determine the corrosion susceptibility of different alloys exposed to continuous fresh seawater. This was achieved by calculating the charge transfer resistance of the metal surface and the resistance of the solution. The total exposure time of the tests was about 180 days. The visual inspection of the tested samples, showed a bio-film formation on the surface of these samples. Also, it was observed that the stainless steel 316, sanicro 28, Cu–Ni 70–30, and titanium alloys exhibited good corrosion resistance.

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1. Introduction

It has been widely known that marine bio-fouling of metal surfaces in contact with seawater is the main cause of several technical problems and economic loss in industry. Marine bio-fouling is defined as the community of organisms found

growing on permanently submerged surfaces of objects in seawater. The growth of this community usually interferes with the efficient use of the surfaces. For example, the organism is known to reduce the flowing of the fluids through the pipe-lines, to reduce the heat transfer in the heat exchanger systems, to reduce the ship's speed and encrusting of the support legs of oil rigs (Mercer, 1990; Bott, 1990). Marine micro fouling is defined as the growth of micro-organisms at metal–solution interfaces. Also, marine micro fouling can be even up to a few micrometers thick. It is known that marine micro fouling reduces heat transfer coefficient in heat exchange systems by as much as 40% besides causing what is known as microbiologically induced corrosion (MIC). Different types of bacteria cause corrosion by various mechanisms ranging from formation of differential aeration cells to production of aggressive

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environments through chemical changes (Carew et al., 1995). It is expected that the seasonal changes in the Gulf seawater will have an effect on the following factors; content of chloride, pH, temperature, oxidizing ability, biological activity, and flow rate, which are controlling the corrosivity of the seawater.

In this investigation, the roles of seasonal changes on the corrosion behavior of different alloys such as: sanicro 28, stainless steel 316, Cu–Ni 70–30, and titanium were investigated by the open circuit potential measurements (OCP) and the electrochemical impedance spectroscopy (EIS) technique. The (OCP) measurements will be used to study the effects of the seasonal change in the Gulf seawater on the corrosion behavior of four different alloys for a period of 6 months under continuous flowing seawater condition. The OCP measurements can predict the overall behavior of the tested alloy under the marine media, and whether the bio-film formation will passivate or activate the surface of each alloy. On the other hand, the EIS experiments will be used to determine corrosion parameters such as the polarization resistance (R_p) which is the most important parameter, for quantitatively studying the corrosion kinetics of metallic materials. Also, the polarization resistance allows for the evaluation of the corrosion current density (I_{Corr}), via the Stern–Geary equation (Beavers et al., 2005):

$$I_{corr} = \beta a * \beta c / 2.303(\beta a + \beta c) * R_p \quad (1)$$

where, βa and βc are the Tafel constants, and assumed to be equal to 120 mV, based on a symmetry factor that equals one, of Tafel's equation (Beavers et al., 2005).

In addition, the EIS technique can be used to provide information about the charge transfer resistance (R_{ct}), the solution resistance of the system (R_{sol}), and the double layer capacitance (C_{dl}).

2. Experimental work

Metallic samples of stainless steel 316L, UNS S31603, (18% Cr, 12% Ni, 2.5% Mo, 2% Mn, and balance of Fe), sanicro 28, UNS S 62800, (27% Cr, 31% Ni, 0.002% C, and balance of Fe), Cu–Ni 70–30 (69% Cu, 30% Ni, 0.5% Fe, and 0.6% Mn) and commercial pure titanium, UNS R50250, (0.2% Fe, 0.18% O, and balance of Ti) were used in this investigation. Those four alloys have been selected in this study because of their common applications in seawater (Beavers et al., 2005). All samples were mounted on a Teflon sample holder. The sample holder was especially designed to seal the samples from the surroundings, except the exposed area of 1 cm². The exposed surface of each material was first cleaned with 5% HCl, and then mechanically polished with silicon carbide paper up to the finest grade, 1200 grit finish. The electrochemical test cell was designed to support the continuous flow of fresh seawater of the Gulf seawater and to facilitate the EIS measurements. The dimensions of the cell were 100 cm in length × 60 cm in height × 40 cm in width. The seawater was pumped from a depth of several meters, of Doha Desalination plant, to storage tanks. Then the seawater was filtered prior to the electrochemical tests. This process was carried out on a frequent basis during the 180 days. Fig. 1 shows the electrochemical cell configuration that allows the continuous flow of fresh seawater. Also, the cell is equipped with a reference electrode which was a saturated calomel electrode (SCE), 241 mV versus

SHE, and a counter electrode which was a graphite rod. Electrochemical impedance measurements were performed using an EG&G impedance analyzer system model 6310, and the software used for analyzing the outputs was EG&G, 398 model. The frequency range used was between 100 kHz to 10 mHz, and the voltage amplitude was ±5 mV root mean square (rms). Each EIS test was obtained after monitoring the open-circuit potential for 1 h. The output data were defined in three graphical formats; the Nyquist, Bode, and admittance formats. From these plots, the charge transfer resistance R_t , solution resistance R_{sol} , and double layer capacitance C_{dl} were calculated manually. A simple Randles circuit was used for interpreting the EIS data. The Randles semi circle was used for data fitting of the experimental results. The acquired data were about 13 tests in 180 days, the temperature of the seawater during the tests varied from 18 °C in winter days to 33 °C in the summer days. The chemical constituents of the seawater are given in Table 1. Also, the resistance of the seawater has an average value of 8 Ω cm².

3. Results and discussion

3.1. Visual inspection

The samples were removed from the electrochemical cell at the end of each test. Then the samples were examined visually. A bio-film was observed to form on the metal surface. The bio-film was in the form of a thin layer spread on the whole surface, around 20–50 μm. Also, there was no sign of a visible corrosion on the samples.

3.2. Electrochemical results

During the tests, the seawater temperatures at the Doha power and desalination plant, fluctuated from 18 °C (in winter days) up to 33 °C (in summer days). This variation in temperature was liable to influence the development of the bio-film on the surface of the examined alloys in two ways; by altering the bacterium population density, and/or by affecting the biological activity of the cells (Shams El Din et al., 2003). The potential–time curve of the examined alloys is given in Fig. 2. The data revealed that, although the examined titanium sample has the highest potential during the test (more negative), but also, the titanium shows that there was no effect of the marine fouling on its potential stability. For the other alloys, (stainless steel 316, sanicro 28, and Cu–Ni 70–30), the potential was shifted up (more positive), on day 40 which was in winter season, and became more positive for the next 20 days. “This can be explained due to the seasonal changes between the winter and summer seasons. In the winter season, the bio-film was observed to have a slow rate of formation on the surface of the tested alloys. On the other hand, in the summer season, the bio-film was observed to have a high rate of formation. The potential of these alloys shifted down (more negative) after 60 days of the test. This was due to the warm up of the seawater (Shams El Din et al., 2003)”. “Also, a similar behavior was observed by the authors on different alloys, namely the stainless steel 304 and Hastelloy G-30, in a separate study (Al-Muhanna and Habib, 2010). It is worth mentioning that there was a shift of the potential of stainless steel 316 and Cu–Ni 70–30 from –350 to –300 mV after 150 days of expo-

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