Available online at www.sciencedirect.com
ScienceDirect

Trans. Nonferrous Met. Soc. China 24(2014) 570−581

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn

Galvanic corrosion behavior of copper/titanium galvanic couple in artificial seawater

Xiao-qing DU[1], Qing-song YANG[2], Yu CHEN[1], Yang YANG[1], Zhao ZHANG[1]

1. Department of Chemistry, Zhejiang University, Hangzhou 310027, China;
2. Zhanjiang Corrosion and Protection Center, Zhanjiang 524000, China

Received 22 January 2013; accepted 31 May 2013

Abstract: The corrosion behaviors of copper and copper/titanium galvanic couple (GC) in seawater were studied by electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques in conjunction with scanning electron microscopy (SEM) method. The results show that the corrosion process of copper in seawater can be divided into two stages, in which corrosion resistance and S_E show the same evolution trend of initial increase and subsequent decrease, while S_G changes oppositely. However, the ensemble corrosion process of copper/ titanium GC in seawater includes three stages, in which corrosion resistance and S_E show the evolution features of initial decrease with a subsequently increase, and the final decrease again; while S_G changes oppositely. The potential difference between copper and titanium in their galvanic couple can accelerate the initiation of pitting corrosion of copper, and both the minimum and maximum corrosion potentials of copper/ titanium GC are much more positive than those of pure copper.

Key words: Cu/Ti galvanic couple; galvanic corrosion; electrochemical impedance spectroscopy; electrochemical noise

---

1 Introduction

Copper and its alloys are widely used in industry, especially in naval construction, heat exchangers, oil transportation and so on [1], due to their good machinability and durability, intricate functionality and low cost [2]. In the design of industrial products, a pure copper material needs to couple with titanium, magnesium, stainless steel or other materials by wire connection [3], welding [4] or other mechanical processing, so as to meet the mechanical and electrical demands [5]. Because the free corrosion potentials of various components are different [5,6], two main metals or alloys can transfer their own electrons through combination, and therefore the galvanic corrosion is inevitable when they are immersed in the seawater [7−9].

Galvanic corrosion is an enhanced corrosion between two or more electrically connected different metals originally [10], where the more active one acts as anode and corrodes, while the less active one is cathode [5]. This will increase the corrosion rate of the anodic metal and reduces that of the cathodic alloy [10]. Up to now, galvanic corrosion is very common in municipal infrastructure and industrial [11], and has been studied by many researchers.

KIRAN [7] predicted the corrosion rate of galvanic corrosion through establishing a numerical model, and verified its accuracy by scanning vibrating electrode technique (SVET) and immersion tests. Many techniques such as mass-loss [6,10], potentiodynamic polarization [12−15] and zero resistance ammeter (ZRA) [15−17] have been adopted to determine the galvanic corrosion parameters, such as corrosion potential and galvanic current. Then some relations, such as the relation of galvanic current with anodic dissolution current and the equation between the corrosion current and polarization potential, were deduced according to those parameters [10].

Most researchers focused on the influence factors of galvanic corrosion. The results show that the galvanic corrosion current increased with the increase of area ratio S_c/S_a [10,18], where S_c and S_a are the areas of cathode and anode respectively; while the research from MUJIBUR RAHMAN et al [4] on galvanic corrosion of laser weldments of AA6061 Al alloy indicated that the

---

Foundation item: Projects (21073162, 51131005) supported by the National Natural Science Foundation of China; Project (Y4100206) supported by the Science and Technology Bureau of Jiaxing Municipality and Zhejiang Provincial Natural Science Foundation of China

Corresponding author: Zhao ZHANG; Tel: +86-571-85615190; E-mail: eaglezzy@zjuem.zju.edu.cn

DOI: 10.1016/S1003-6326(14)63097-1

galvanic corrosion current increased with either the accumulation of intermetallic phase or the increase of corrosion surface area. The influence of temperature is complicated. Generally, the galvanic corrosion current increases with the corrosion temperature [16,19]. In addition, the factors such as the flow velocity of the medium [14,18,20], the dissolved oxygen content [21], pH [22] and the distance between electric dipoles [23,24] have also been studied. As to the materials and medium, the researchers paid much more attention to the galvanic corrosion of Mg alloy [25,26], Al alloy [27], steel [28] in the solutions containing Cl^-, S^{2-} [15] and Br^- [29].

This work aims to research the galvanic corrosion behavior of electric couple made of copper and titanium, being immersed in seawater for a long time at 25 °C, as the early researches were mostly focused on corrosion for a short time, which could not give any information about the exchange of anode and cathode in a galvanic couple. Electrochemical impedance spectroscopy (EIS), electrochemical noise (EN) and scanning electron microscopy (SEM) techniques are adopted to analyze the reaction resistance, corrosion product layer, galvanic potential and corrosion morphologies.

2 Experimental

2.1 Material and specimen preparation

The rod specimens of 0.40 cm in diameter were cut from copper rod. Then the specimens were connected respectively to a copper wire at one end, sealed using nylon with the other end exposed as the working surface. Before experiments, the working surface was polished with abrasive papers through 500−1200 grade and velvet, washed with twice distilled water, and finally degreased with acetone.

Special coupled electrodes for experiment were prepared by embedding copper column into the titanium cylinder with inner and outer diameters of 0.40 cm and 0.56 cm respectively, then the couple was encapsulated with nylon, and the exposed area of each metal was equal to 0.13 cm^2.

2.2 Measurement methods

EIS tests were recorded with an impedance measurement apparatus (PARSTAT 2273, Advanced Electrochemical System) at the rest potential, the applied sinusoidal voltage amplitude was 5 mV and the sweep always initiated from the frequency of 100 kHz to 0.01 Hz. The tests were performed at different immersion times in a conventional three-electrode compartment cell. The rod copper or the coupled copper/ titanium specimen prepared in section 2.1 was the working electrode, a large platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) was employed as the reference.

EN was monitored as a function of time between the working electrode and SCE with a Powerlab/4s apparatus (e-DAQ), which was controlled by Chart4 software using the Windows XP operating system. This equipment allows resolutions of 1 μV for voltage signals and 1 pA for current signals. EN data of 4096 points were collected at 4 point/s each time, under which a frequency window was defined in which most usual corrosion processes can be detected. The analytical results for maximum entropy method (MEM) technique were obtained by specific data technique.

All tests were carried out in artificial seawater (pH 7.5) whose main components are listed in Table 1 at room temperature (25±2) °C. During the above experiments, the corrosion morphologies of the samples were observed at different immersion time using a JEOL USA JSM−5510LV scanning electron microscope (SEM) with a field emission gun operated at 3 kV.

Table 1 Chemical compositions of seawater

$\rho(Cl^-)$/ $(mg \cdot L^{-1})$	$\rho(Br^-)$/ $(mg \cdot L^{-1})$	$\rho(CO_3^{2-})$/ $(mg \cdot L^{-1})$	$\rho(SO_4^{2-})$/ $(mg \cdot L^{-1})$
20237.2	72.9	1066.3	3237.2
$\rho(Na^+)$/ $(mg \cdot L^{-1})$	$\rho(K^+)$/ $(mg \cdot L^{-1})$	$\rho(Mg^{2+})$/ $(mg \cdot L^{-1})$	$\rho(Ca^{2+})$/ $(mg \cdot L^{-1})$
11131.5	423	1366.6	650.4

3 Results and discussion

3.1 Corrosion behavior of copper

In order to elucidate the galvanic corrosion behavior of the coupled copper/ titanium in seawater, the corrosion behavior of copper has been first investigated using EIS and EN techniques.

Figure 1 shows the typical EIS evolution features of copper corrosion in seawater. With the help of both the features of the EIS diagrams (such as the number and the width of the phase angle peak of the peak in Bode plots and the number of the capacitance loops in Nyquist plots) and the method developed by WEIJDE et al [30] and CAMPESTRINI et al [31] simultaneously, two time-constants of the EIS plots can be determined. The equivalent electrical circuit (EEC) shown in Fig. 2 has been adopted to fit the EIS plots by Z-view software. In Fig. 2, R_s is the solution resistance, CPE1 is the capacitance of outer passivating film and corrosion product layer, R_2 is the membrane resistance of outer passivating film and corrosion products, CPE2 is the double layer capacitance and R_3 is charge transfer resistance. And the analysis results are listed in Table 2.