Effect of tin on the corrosion behavior of sea-water corrosion-resisting steel

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ABSTRACT

This paper investigated the effect of tin on the corrosion resistance of tin-containing steel and tin-free steel using electrochemical measurements in seawater. Results showed that tin-containing steel had lower corrosion current and higher impedance than tin-free steel. Surface analyses of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) indicated that tin could form SnO_2 and SnO in rust layer, and both of them could improve impedance and corrosion resistance of rust layer. Besides, the coprecipitation process of tin oxides with iron oxides could make the rust layer more uniform and compact, which could make the tin-containing steel have better corrosion resistance than tin-free steel. Secondary ion mass spectrometer (SIMS) showed that there was no obvious segregation of tin on substrate steel when tin addition was 0.038 wt.%, and tin could improve the oxidation resistance of substrate steel evenly by lowering the steel's Fermi energy from -9.276 eV to -14.445 eV.

1. Introduction

Currently, the development of ocean energy has become a focus point around the world, which provides a huge marketing demand for the steel used in ocean engineering. Therefore, there would be a great potential to develop steel with low cost and outstanding corrosion resistance to seawater. Many countries have developed sea-water corrosion-resisting steel, such as Mariner steel of America, Aps20A steel of France and Mariloy steel of Japan, which belongs to Ni–Cu–P series, Cr–Al series and Cu–Cr–Al series, respectively. Normally, chemical composition and microstructure are regarded as principal influence factors of corrosion resistant property. Corrosion resistant properties of frequently-used elements such as Copper, Aluminum, Chromium, Molybdenum and Nickel have been investigated in lots of published literature [1–10], and their function on corrosion resistance has been learnt by people. Nowadays, people started to pay more attention to the effect of tin element on corrosion resistant property, especially after the successful development of high-tensile corrosion resistant steel containing tin in Japan in 2011.

The low melting point of tin will has a negative impact on billet thermoplastic, which can adversely affect hot workability during manufacturing process. But on the other hand, tin itself has excellent corrosion resistance [11], and it was reported that a small content of tin (about 0.05 wt.%) could improve the corrosion resistance of steel [13], so the cost of steel would be reduced if tin was added into steel

acting as a corrosion resistant element. Some researchers have pointed out the positive impact of tin on corrosion resistant property when tin is added into steel [12–14]. Nguyen Dang Nam and A. Pardo [12,14] introduced a conclusion that the corrosion rate decreased with the increasing content of tin, and the addition of tin had a positive effect on pitting corrosion resistance of steel as well. Particularly, A. Pardo and M.C. Merino [13] reported that Cu could favor pit nucleation but inhibit its growth, whereas Sn exerted an opposite effect, i.e. favoring pit growth and inhibiting its nucleation. Wenjin Zhang [4] reported that the corrosion resistance of Mg–Zr–Ca alloy was improved apparently with the addition of Sr and Sn. However, these studies just referred some phenomena. The impact of tin on corrosion resistant properties in mechanism and essential aspects had not been discussed. Besides, the previous investigations were mainly based on stainless steels or steel under acid corrosive environment, and till now no research has been made to investigate the effect of tin on corrosion resistant property of low alloy steel in seawater environment.

This paper attempts to evaluate the effect of tin on corrosion resistant properties in sea-water corrosion-resisting low alloy steel. After the accelerated corrosion test, the corrosion resistant properties of the two steels were characterized by potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) measurements. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were conducted to analyze the corrosion products. Secondary Ion Mass Spectroscopy (SIMS) was also used to ascertain the distribution of tin on substrate steel. Besides, the cross section of corroded sample was observed using Scanning electron microscope (SEM).

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2. Experimental

2.1. Materials and test solution

All the specimens were cut from industrial plates with the thickness of 20 mm, which were processed by thermo mechanical control process (TMCP) technology. Table 1 shows the chemical compositions of the two investigated steels. Results of optical microscopy observation of the two steels are shown in Fig. 1, which indicate that the microstructures of both these two steels are ferrite–pearlite. Thus the effects of different microstructures between the two steels on corrosion behavior can be neglected.

The electrochemical test specimens had a dimension of 10 mm × 10 mm × 3 mm, whereas those for the immersion tests had a dimension of 60 mm × 30 mm × 5 mm. The solution used to simulate seawater was prepared according to GB/T 19746-2005, with pH ranging from 8.2 to 8.4. Specifically, per liter of this solution contained 24.534 g NaCl, 4.094 g Na_2SO_4, 0.020 L standard solution A and 0.010 L standard solution B. The chemical compositions of standard solution A and B are listed in Table 2. The test temperature was controlled at 28 °C to accelerate the corrosion process [15].

2.2. Weight loss test

The weight loss measurements were performed according to GB/T 16545-1996. The exposed surface area (60 mm × 30 mm × 5 mm) of each specimen was polished with 1000-grit silicon paper, then cleaned in an ultrasonic bath with ethanol for 5 min and dried in hot air.

After the initial mass was measured, the specimen was immersed in the test solution for 1 day. After the test, each specimen was cleaned with distilled water, then pickled in a solution of 500 ml HCl + 3.5 g hexamethylene tetramine + balanced distilled water for 5 min to remove the products of the corrosion. These were then degreased in an ultrasonic cleaner with ethanol for 5 min, followed by a cleaning with distilled water and drying in hot air. The final mass of the tested specimen was measured for the weight loss test. Besides, the processes of specimen preparation and rust cleaning were also used to observe the morphology after removing corrosion products.

2.3. Potentiodynamic polarization test

The exposed area of specimens was 10 mm × 10 mm with 100 mm^2 area, and the other sides were embedded in epoxy resin. Before the potentiodynamic polarization tests, all the specimens were grinded with 1000-grit silicon paper and then were polished to get a flat and glabrous surface. Then the potentiodynamic polarization tests were conducted on specimens after 1 day pre-corrosion in seawater.

During the electrochemical tests, all specimens were completely immersed in 600 ml seawater at temperature of 28 °C. Electrochemical measurements were carried out using a three-electrode system with saturated calomel electrode as reference electrode, Platinum electrode as auxiliary electrode and the sample as working electrode. The polarization measurement started from a potential of +250 mV (SCE) and ended at a potential of −250 mV (SCE) versus the open circuit potential. The scanning rate was 0.2 mV/s during polarization curve measurement.
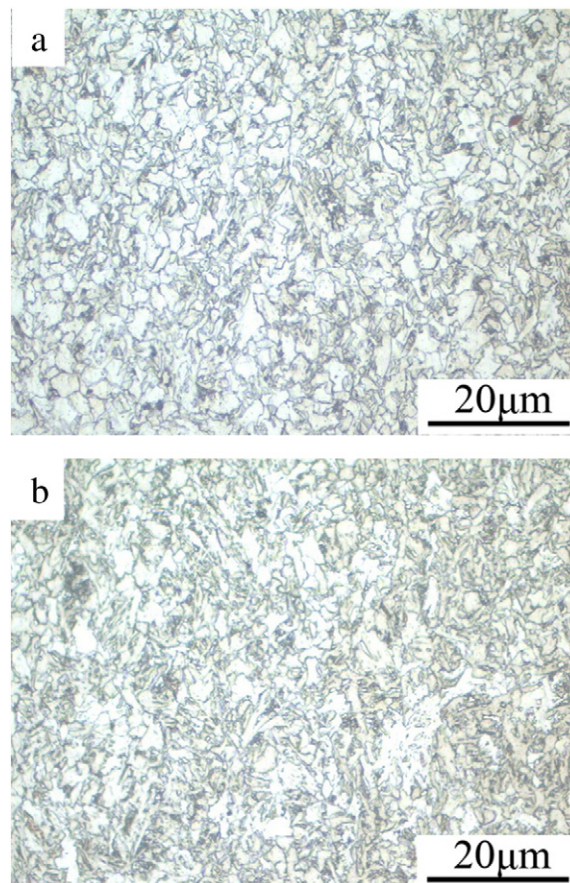

Fig. 1. Microstructures of two steels. (a) Tin-containing steel, (b) Tin-free steel.

2.4. Electrochemical impedance test

The specimens used for electrochemical impedance tests were the same as those used for potentiodynamic polarization tests. A three-electrode system was used in EIS measurement. The test parameters were as follows: 10 mV perturbation and five points per decade. Frequency range was from 100 kHz to 10 mHz. Before EIS test proceeded, the potential of specimens reached a stable state in the solution. The experimental results were interpreted based on an equivalent electrical circuit by using a suitable fitting procedure of ZSimpWin.

2.5. Corrosion products and elements test

The corrosion products obtained from different corrosion cycle were examined by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), which could identify the relationship between corrosion products and corrosion behavior. The specimens of XPS and XRD were powder.

Besides, distribution of elements on the substrate steel was investigated by Secondary Ion Mass Spectroscopy (SIMS). SIMS was performed with a camera ION-TOF GmbH ion microscope. Direct-ion images with size of 100 um × 100 um were acquired using a resistive anode encoder

Table 1
Chemical compositions of specimens (wt.%).

Specimen	C	Si	Mn	P	S	Sn	Cu	Cr	Al
Tin-free steel	0.060	0.300	1.100	0.017	0.003	–	0.490	0.500	0.035
Tin-containing steel	0.060	0.280	1.000	0.015	0.003	0.038	0.500	0.520	0.034