Passivation of Zinc Anodes in Marine Conditions

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Weather buoys are used for measuring meteorological data at sea and sending that data to coastal stations via a wireless network. Located under the buoy is a heavy ferrous metal counterweight box for balance and stability. This buoy counterweight is protected against corrosion by zinc sacrificial anodes. After about six months of operation, some of the anodes are sacrificed, while others are not, apparently because they experienced passivation. Test results show that the nonsacrificed anodes contain iron impurities and intermetallic phases in their microstructures. Thus, a simple anode acceptance test is the observation of impurities and intermetallic phases in the zinc anodes.

A weather buoy is a floating object at sea with the capability to gather and transmit data. The data collected include wave height and direction; velocity, temperature, and salinity of seawater; wind speed and direction; and sea and atmospheric temperatures. To fix the position of the buoy, it is connected to the sea bed with a metal chain. To balance the buoy and maintain its vertical position, a heavy ferrous box filled with lead is attached to the bottom. Zinc anodes are used for cathodic protection (CP) of the metal box. Figure 1 shows the metal box attached to the buoy and the zinc anodes on the metal box. Figure 2 shows the condition of the anodes after about six months in seawater. Some anodes have been sacrificed, while others have not. To explain this discrepancy and to develop a rapid method for rejecting delivered anodes that will not sacrifice, a series of tests was performed.

Test Approaches and Results

Surface Layer Examination

An ohmmeter was used to investigate the electrical connection between the nonsacrificed anode surface layers and their ferrous metal cores. No electrical connection was identified, and it appears that a nonconductive or passive layer had formed on these anodes as a result. The passive layer prevented these anodes from functioning sacrificially as part of the CP system. Only the anodes that remained active provided CP current.

Figure 2 also shows that the anodes were connected to the metal box with bolts. This method of connection is inappropriate for the seawater environment. Anode cores should be connected by welding or both bolting and spot welding.[1] After removing the bolts, a brown iron oxide was found between the metal core of each nonsacrificed anode and the body of the metal box. This oxide had increased the electrical resistance between the nonsacrificed anode core and the metal box.

Chemical Analyses and Microstructure

Chemical analyses of the nonsacrificed and sacrificed anodes were determined by an optical emission spectrometer (OES). Table 1 shows very similar chemical analyses for the two anode types. An investigation of the microstructure of the nonsacrificed and sacrificed anodes with metallographic etchant (a mixture of 100 mL distilled water, 20 g chromium trioxide [CrO_3] and 3 g sodium sulfate [Na_2SO_4]) found phases with a regular shape in the microstructure of the nonsacrificed anode that did not appear in the sacrificed anode (Figure 3).

The next investigation used an energy-dispersive x-ray spectroscopy (EDS) with a scanning electron microscope (SEM) to determine the chemical analyses of the regular-shaped phases. As shown in Figure 4, chemical analyses of a regular-shaped phase and the zinc background were conducted at Points 1 (regular phase) and 2 (background), respectively. According to the EDS results, a significant percentage of the material at Point 1 was iron, but no iron was indicated at Point 2 (Table 2). Iron impurities have deleterious effects on the behavior of zinc anodes. Fe ions can form intermetallic compounds with zinc that promote passivation of zinc anode surfaces in seawater.[1-4]

Conclusions

The electrochemical behavior of zinc anodes in seawater depends largely on the presence of iron impurities. When the amount of iron impurities in a zinc anode exceeds its solid solubility in zinc, the iron can form intermetallic compounds, which promote passivation of the zinc surfaces. These appear as separate phases with a regular shape in the zinc background. Therefore, in addition to electrochemical tests, anode metallography can be used as an accelerated test for quality control of zinc anodes before installing them in seawater.

It was found that bolted connections of anode cores to the ferrous buoy counterweight boxes is unsuitable for service in seawater. Welded connections are much more reliable for avoiding the formation of oxide layers, which increase the circuit's resistance.

Acknowledgments

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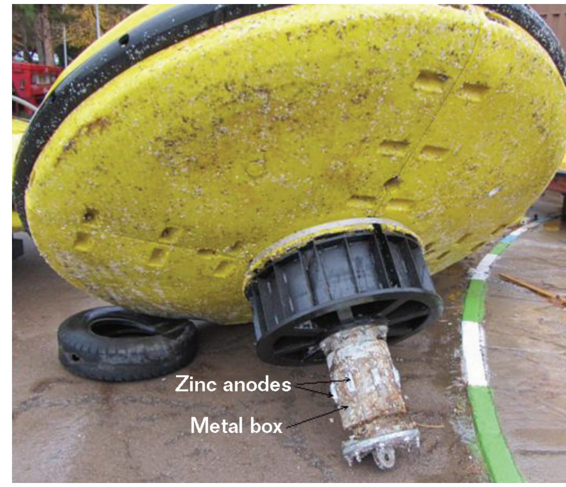

FIGURE 1 Zinc anodes are used for CP of the buoy's counterweight (metal box).

FIGURE 2 Sacrificed and nonsacrificed zinc anodes after six months of immersion in seawater.

TABLE 1. CHEMICAL ANALYSES OF NONSACRIFICED AND SACRIFICED ANODES, MEASURED BY OPTICAL EMISSION SPECTROMETER

Anode	Zn	Pb	Mg	Al	Cd	Cu
Nonsacrificed	99.53	0.0993	0.0011	0.279	0.0236-0.0135	0.197-0.104
Sacrificed	99.22	0.0201	0.0011	0.573-0.109	0.0127-0.0008	0.175-0.0423

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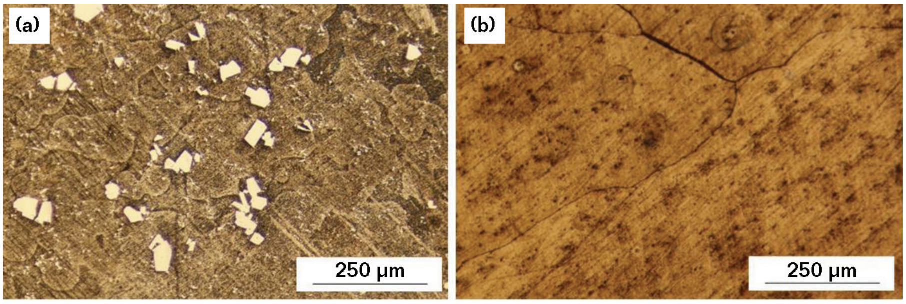

FIGURE 3 Microstructure of the zinc anodes, (a) nonsacrificed anode and (b) sacrificed anode, etched with 100 mL distilled water, 20 g CrO_3 and 3 g Na_2SO_4.

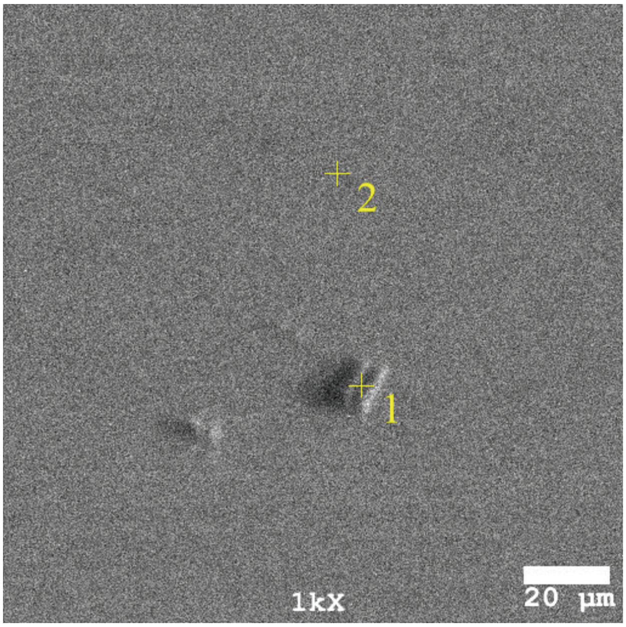

FIGURE 4 In Points 1 and 2 of the nonsacrificed anode's microstructure, chemical analyses were measured by EDS using a SEM.

TABLE 2. CHEMICAL ANALYSES OF POINTS IN FIGURE 4

Element	Line	Intensity (c/s)	Atomic (%)	Concentration (wt%)
Point 1				
O	Ka	84.79	33.86	11.90
Fe	Ka	363.88	33.15	40.69
Zn	Ka	182.14	32.99	47.41
Total			100.00	100.00
Point 2				
O	Ka	38.82	15.67	4.52
Al	Ka	35.76	5.84	2.85
Zn	Ka	549.71	78.49	92.63
Total			100.00	100.00