

Dezincification of Epoxy Coated Brass in Cochin Estuary, India

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Abstract— Inhibited α brasses are largely immune to dezincification in most water, but the effect of tin and arsenic addition to α/β brasses is not so reliable or predictable in controlling the problem. There have been many cases of dezincification in duplex brasses in both fresh water and seawater. There is no reliable method of inhibiting the dezincification of two-phase brass despite there are some protection methods such as inhibitors, electro deposition and electro polymerization. Organic coatings are effectively used for the protection of metals due to their capacity to act as a physical barrier between the metal surface and corrosive environment. Hence, epoxy coating on brass was applied and effect of this against dezincification in Cochin estuarine water over a period of one year was studied and reported in this paper.

Index Terms— Dezincification, open circuit potential, biomass.

I. INTRODUCTION

Different types of corrosion can occur to the structures, ships and equipments made up of copper and copper based alloys when exposed to seawater, which is a good electrolyte that can cause corrosion. Brass possesses attractive properties, namely good corrosion resistance, mechanical workability, excellent electrical and thermal conductivities and good resistance to bio fouling. Corrosion resistance of brass has been attributed to a protective cuprous oxide layer formed upon exposure. However, this alloy can deteriorate due to the local gradient of pH and oxygen under seawater condition and distinctive attacks are impingement attack, dezincification of brasses and pitting.

The dezincification of brass is one of the most recognized forms of selective corrosion and it has attracted the attention of researchers for the last two decades. The survey of literature clearly indicates that many of the dezincification mechanistic studies were performed in noncomplex media and hence their conclusions cannot be extended to estuarine water, which is of great significance in connection with the extensive use of brass in marine environment. It is particularly relevant to Cochin region where various industries extensively use brass in marine application in the form of condenser, pipe work, valves, screws, and nuts and bolts. Epoxy-resin-based paints generally offer very good corrosion-protective properties and are widely used in harsh environments such as the seawater. They are two-pack

systems, the curing agent normally used being polyamines or polyamides [1]. The corrosion behavior of epoxy-poly amide primer attached to galvanized steel was assessed coatings [2] and they found that the corrosion resistance was increased with epoxy coating [3]. The epoxy coated steel in tidal zone provided better anti-corrosion ability than polyurethane resin and acrylic resin [4]. The modifying the surface of brass with polysiloxane coating decelerates general corrosion and hamper selective dissolution and its protective effect is based on shielding the alloy surface [3]. The effectiveness of sol-gel organic and inorganic hybrid coatings as barrier coating on brass and they found that the coating delayed corrosion on brass [5].

Inhibited α brasses are largely immune to dezincification, but the effect of tin and arsenic addition to α/β brasses is not so reliable or predictable in controlling the problem. There have been many cases of dezincification in duplex brasses in both fresh water and seawater. There is no reliable method of inhibiting the dezincification of two-phase brass despite there are some protection methods such as inhibitors, electro deposition and electro polymerization. Organic coatings are effectively used for the protection of metals due to their capacity to act as a physical barrier between the metal surface and corrosive environment. The dezincification behavior of epoxy coated brass of the present study highlights in terms of following factors such as corrosion rate, biomass, open circuit potential and dezincification factor.

II. MATERIALS AND METHODS

A. Sample preparation and exposure test:

Epoxy coating was applied on pre treated brass panels by a brush and allowed to cure at 30^o C to get dry film thickness of 100 ± μ m. The epoxy-coated brass panels for immersion were taken in 12 triplicates. The panels were weighed and fixed on fiberglass strips with PVC nuts and bolts and immersed in estuarine water at the far end of jetty which belongs to School of Marine sciences, Cochin University of Science and Technology (3 m depth and 1m above the estuarine bed). At high tide the water depth in the selected site was 4 m deep and at low tide the water depth was 2 m and so the brass panels were always below water surfaces at least by 1 m. At the end of each exposure month, panels were retrieved one after another. After retrieval the panels were first rinsed gently with fresh estuarine water to remove any non-adhering bacteria and diatoms.

B. Weight change method

The difference between initial weight prior to deployment and final weight, before corrosion products were removed,

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was used for calculation of weight gain for plain brass. The difference between initial weight prior to applying of coating and final weight, after removal of epoxy coating with out removal of corrosion products underneath the coating was used for calculation of weight gain for epoxy coated brass. At the end of each exposure period, the coatings were removed first by the epoxy diluents (butyl glycidyl ether) and then mechanically using an acrylic knife.

The corrosion rate of epoxy-coated brass was calculated by the difference between initial weight prior to applying of coating and final weight, after the corrosion products removed by standard method. The following equation was used for corrosion rate measurement.

$$mdd = W / (A * T) \quad (1)$$

where mdd is the corrosion rate expressed in terms of metal loss (mg)[per decimetre square area per day], W the loss in weight (mg), A the area of panels (dm²), and T the exposure time (days).

C. Open circuit potential measurement:

The open circuit potentials of epoxy coated brass immersed in estuarine water in a flask connected to the reference electrode via a KNO₃ salt bridge were measured exposure- wise with a digital multimeter.

D. Dezincification factor:

During the above test period, the concentration of Cu²⁺ and Zn²⁺ in the solutions after each measurement was determined by atomic absorption spectrometer. Using the Cu²⁺ and Zn²⁺ concentration and Cu and Zn in brass alloy, dezincification factor (Z) was calculated according to the following equation:

$$Z = (Zn/Cu)_{sol} / (Zn/Cu)_{alloy} \quad (2)$$

where (Zn/Cu)_{sol} is the ratio between Cu²⁺ and Zn²⁺ ions in solution and (Cu and Zn)_{alloy} is the ratio between the two elements in the alloy.

E. Assessment of fouling:

Fouling on brass panels and epoxy coated brass were assessed, exposure-wise, in terms of biomass. Biomass was calculated after scrapping the mass adhered on the metal surface and drying in a air oven for an hour at 60°.

III. RESULTS A DISCUSSION

A. Corrosion rate and biomass

The Corrosion rate of epoxy coated brass sample immersed in estuarine water, Cochin at each exposure period is shown in Fig 3.1.

The corrosion rate was found to be 3.33 mdd for Sep-07 and Oct-07 and then reduced to 1.11 mdd and afterward reached 1.33 mdd on June-08 with minor fluctuation in between. Then reduced to 0.41 on Aug-08. The decrease of corrosion rate implies that the combined action of accumulation of biomass and epoxy coating on brass as a barrier between the metal interface and seawater reduce the diffusion of oxygen and possess excellent resistance when uniform corrosion is considered. The reason for lower

corrosion rate of epoxy-coated brass could be ascribed to the adherent epoxy coating and also the lower levels of dissolved oxygen concentration. The corrosion products remained on brass does not allow the corrosion to progress and portion of areas exposed to estuarine water undergone corrosion.

The instantaneous corrosion rate varies strongly with time and depends on the composition of the electrolyte [6]. It was found that increasing oxygen concentration causes rapid increase in corrosion rate [7]. The corrosion rate increases as interfacial contamination increases while non-contaminated surface are free of corrosion [8]. Higher dissolved oxygen content will increase in the rate of attack and lead to the higher risk of corrosiveness [9].

Biomass on brass sample immersed in estuarine water, Cochin at each exposure period is given in Fig. 3.1.

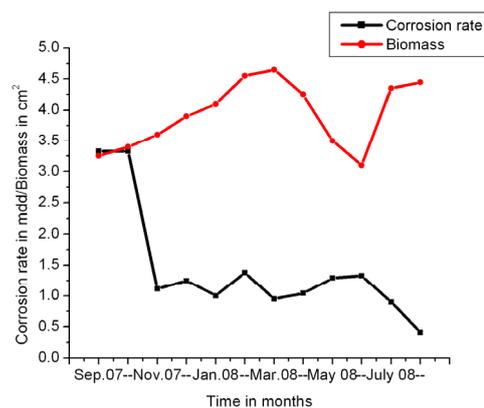


Fig. 3.1 Corrosion rate and biomass of brass panels in Cochin estuary at each exposure period

Biomass on brass was 3.25 g/cm² on Sep-07 and increased to 4.65 g/cm² on Mar-08 and reduced slightly to 3.1 g/cm² on June-08 thereafter increased to 4.45 g/cm² on Aug-08. In increase of biomass up to Mar-08 indicates that there is no relationship between bio fouling and corrosion. Earlier studies carried out in mandapam coastal water on ferrous materials revealed that higher corrosion on the coupons without fouling than coupons with the presence of fouling [10]. The accumulation of these biological organisms is dependent on specific environmental conditions. Conditions which are most conducive to their development are relatively shallow water such as in a harbor, b) warm temperatures, c) low seawater flow, and d) smooth, hard surfaces [11].

B. Open circuit potential

The open circuit potential of epoxy coated brass sample immersed in estuarine water, Cochin at each exposure period is given in Fig 3. 2.

The experimental results showed value of -0.15 Vs. SCE On Sep-07 and then decreased to -17 on Oct-07 and thereafter it was increased to -0.21 Dec-07 and -0.2 for Jan-08 and Feb-08 and then sustained at this potential up to Aug-08.

The negative shifts of potential from Sep-07 to Dec-08 indicate the fact that there can be localized corrosion. The positive shift of potential after Dec-08 and sustainable noble potentials (more positive values) mean that brass retains its normal corrosion resistance. Though the OCP of both the systems have decreased over the period of time. The more

negative potentials were noticed for the brass than the epoxy-coated brass.

The open circuit potential, anodic polarization curves and AC impedance spectroscopy and electrochemical measurement of Poly (o-anisidine) coated brass electrodes showed that POA films provided a physical barrier property to brass electrode [12].

The corrosion potential in combination with other methods can provide information about the mechanism of the reaction and the rate controlling process [13]. He concludes that the movement of the corrosion potential in the active (i.e. more negative) direction indicates that the cathodic/anodic areas ratio decreases and as a consequence the underfilm corrosion process may be significant, denoting a limited coating life.

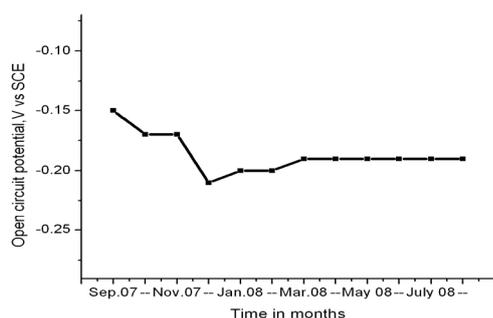


Fig. 3.2 Open circuit potential of epoxy coated brass panels in Cochin estuary at each exposure period

Selective dissolution of zinc occur with no detectable level of copper dissolution below -300V vs Ag/AgCl in 3.4% NaCl and at more noble potential (above $-260\text{Mv Vs. Ag/AgCl}$), dissolution of both components observed at rates which increased as the potential to more noble direction. It is also shown that chloride ions promote the dissolution of both zinc and copper from the alloy [14].

The potential of the coating system closer to the corroding steel indicating the loss of barrier action of the coating [1]. The free corrosion potential of the specimen becomes more anodic when the solution is deaerated, the E_{corr} of muntz metal changes from -235 Mv SCE to -380 mV CE . It is reasonable to assume that this simulates the differential aeration cell formed once it has become porous [15].

C. Dezincification factor

The percentages of leaching of zinc from the matrix of brass was minimum of 1.1 on Feb-08 and maximum of 8.2 on Dec-07 and leaching of zinc has not increased with respect to time of exposure. The percentage of leaching of copper from the matrix of brass was minimum of 8 on Apr-08 and maximum of 23 on Aug-08. Dezincification factor for brass as a function of exposure time is given in Fig.3.3 Dezincification factor higher than one means preferred dissolution of zinc. In all the exposures period, the dezincification factor is less than one, which indicates that dissolution of zinc has not occurred from the matrix of brass for all months. But dissolution of copper has occurred from the matrix of brass in all months. The results is in tune with corrosion rate values of epoxy coated brass. In general, the dezincification has occurred for plain brass except Sep-07 and Oct-07 and dissolution of copper occurred for epoxy

coated brass for all months over exposure.

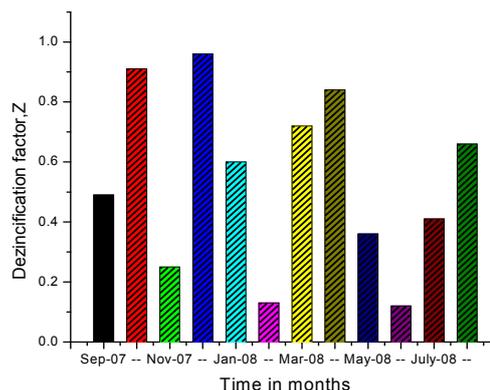


Fig. 3.3 Dezincification of epoxy coated brass panels at each exposure period in estuarine water, Cochin

The abnormal behavior can be due to the synergistic effects of biofilm consortia (aerobic and anaerobic) absence of oxygen at the interface affected by barrier action of epoxy coating during the study period. These phenomena call for detailed further investigation.

IV. CONCLUSION

The decrease of corrosion rate implies that the combined action of accumulation of biomass and epoxy coating on brass as a barrier between the metal interface and seawater reduce the diffusion of oxygen and possess excellent resistance when uniform corrosion is considered. The antifouling property of brass is lost over all months resulting in macro fouling. The open circuit potential of epoxy coated brass shifted to more negative values with respect to time till Dec-07month and then shifted to positive value. The presence of epoxy coating on brass experienced less negative potential than the bare brass. The dezincification factor is less than one for all the exposure. This implies that dissolution of zinc has not occurred from the matrix of epoxy-coated brass from all the exposure.

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