Effect of Pretreatment Temperature on Protection of 70/30 Brass with Benzotriazole

Takenori NOTOYA* and George W. POLING**

Corrosion protections afforded by pretreating 70/30 brass in aqueous benzotriazole solutions at temperatures ranging from 25°C to 100°C was evaluated. Electrochemical characteristics of pretreated brass mirrors were monitored using rapid polarization technique. Thicknesses of surface films were estimated by infrared multiple reflectance spectroscopy. Topography of corroded surfaces subsequent to test exposures was examined by scanning electron microscopy. Both corrosion current densities and corrosion rates indicated that protectiveness of benzotriazole complex films formed on 70/30 brass increased with increasing both pretreatment temperature and its period.

1 Introduction

Benzotriazole (BTA) is one of the most widely used and most effective corrosion inhibitors for copper and copper base alloys in both aqueous and atmospheric environments. The BTA is also an effective inhibiting additive in protective coatings such as in lacquers and in paints. In these coating systems the inhibitor prevents tarnishing beneath the transparent polymeric coatings.

Cotton and Scholes^{1,2)} and Poling and Ogle³⁾ attribute the protective action of BTA to the formation of a semipermeable Cu-benzotriazolate (CuBTA) polymeric complex formed on the metal surface. This invisible polymeric complex film presumably reinforces the copper oxide film normally present on the metal surface. These thin films consist of chemisorbed monomolecular layers plus multilayers of CuBTA which have nucleated and grown epitaxially on the chemisorbed films. Further, the pH of BTA solution which controls the thickness of the CuBTA film has been determined⁴⁾. Recently film thicknesses of the CuBTA on copper were found to increase with increasing pretreatment temperature in the thin film region.

Brasses have been used extensively for many

years under a variety of corrosion conditions. The existing data on brass inhibition by pretreatment with BTA, however, are meager. The purpose of the present study is to compare the protectiveness of CuBTA films formed on 70/30 brass in the aqueous BTA solution at different temperatures. In addition, practical surface treatments of brasses with the BTA solutions were evaluated.

2 Experimental

2.1 Brass specimens

The composition of the 70/30 brass used is; Cu 68.5, Zn 31.4 and Fe 0.05 by weight %. Plates of 70/30 brass were milled to the size of 58×20×2 mm and 45×20×2 mm. The specimens were mechanically polished to No. 1000 emery paper for corrosion test. For surface observation the specimens were further polished with a 1 μ diamond paste followed by electropolishing in an orthophosphoric acid electrolyte (H₃PO₄/H₂O=2 in volume ratio). The BTA used was reagent grade and supplied by K & K Laboratories, Inc.

2.2 Electrochemical Polarization

Rapid galvanostatic anodic and cathodic polarization of the brass specimens was carried out by applying a direct current stepwise every 1 sec to the brass using a Pt auxiliary electrode. The potential of the brass specimen was measured against a saturated calomel reference electrode. Variation of electrode potential was recorded on Polaroid film using an oscilloscope.

* Department of Metallurgy, Faculty of Engineering, Hokkaido University (Sapporo)

** Department of Mineral Engineering, The University of British Columbia (Vancouver 8, B.C., Canada)

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2.3 Infrared spectroscopy

Spectra of CuBTA films formed on 70/30 brass mirrors were recorded on a Perkin-Elmer Model 521 infrared spectrophotometer by means of 9 reflections at 70° incidence. Thickness of the CuBTA films on 70/30 brass, d , was calculated from the relation⁶⁾.

$$d(\text{\AA}) = (7.70 \times 10^3 / N^2) \Delta R / \nu / K$$

where ΔR is the fractional change in reflectivity at the band maximum, N is the refractive index of CuBTA film ($N=1.6$), K is the adsorption constant of the film ($K=0.27$), and ν is the position of the absorption band in wave numbers ($\nu=745 \text{ cm}^{-1}$)³⁾.

2.4 Corrosion test

Pretreatment of the brass specimens was carried out by immersion in an aqueous solution of 0.01 M BTA at five different temperatures for 1, 3 and 30 minutes. Then, the brass specimens were washed thoroughly with distilled water to remove unreacted BTA. The protection afforded these pretreated brass specimens was tested by immersion in aerated 3% NaCl solution for 5 hours and 1 day. The initial pH of the NaCl solution was 5.8. Corrosion rate was estimated from amount of Cu and Zn ions dissolved in the test solutions. The amount of Cu and Zn ions in the test solution were analysed by a volumetric titration using a standard aqueous solution of 0.001 M disodium ethylene diamine-tetra acetic acetate as a titrant (EDTA) with 1-(2-pyridylazo)-2-naphthol as an indicator.

2.5 Scanning electron microscopy

The topography of the 70/30 brass specimen surfaces was examined using an ETEC Autoscan U-1 scanning electron microscope.

3 Results and Discussion

3.1 Corrosion rate

Figure 1 shows corrosion rate of pretreated 70/30 brass in aerated 3% NaCl solution at a stagnant condition as a parameter of the pretreatment periods of 1, 3 and 30 minutes. The corrosion rate decreased logarithmically with increase of both the pretreatment temperature and its period at the temperatures below 60°C while it decreased slightly above 60°C. This fact can be compared with the results previously obtained on pretreated copper of which corrosion rate decreased more pronounced with increasing

Fig. 1 Dependence of pretreatment temperature and its period of time on brass corrosion rate in aerated 3% NaCl solutions of pH 5.8 at 25°C

Fig. 2 Change of inhibition efficiency with pretreatment temperature at three different pretreatment periods

the pretreatment temperature up to 100°C³⁾. Accordingly inhibition efficiency also increased with increasing pretreatment temperature as well as pretreatment period up to 60°C and maintained the value up to 100°C, as shown in Fig. 2. The maximum inhibition efficiency attained by the pretreatment was 73% in a 5 hour-exposure test. The same effect of the pretreatment temperature was also obtained in 1 day-exposure test.

Brownish yellow tarnishing films produced on the non-pretreated brass within 30 minutes in the aerated solutions and later the tarnishing film turned into dark blue in color. On the other hand, no tarnishing films produced on the pretreated brass surface even after 2 days exposure to the solution, and white cloudiness appeared partly instead of the tarnishing film. This fact indicates that dissolution initiates at active sites and thus defects in the CuBTA films. The active dissolution sites were mainly located along the grain boundaries, and the rest of the surface was still protected by the remaining CuBTA films after dissolution occurs, as described later.

Average thicknesses of the CuBTA films formed at different temperatures in the 0.01 M BTA aqueous solution are listed in Table 1.

Table 1 Average thickness of CuBTA films formed on 70/30 brass

Pretreatment temperature (°C)	CuBTA film thickness (Å)
25	20±4
40	31±11
60	36±14
80	42±11
100	51±12

These CuBTA film thicknesses are the average of the five values of CuBTA film thicknesses. The CuBTA films formed under the same conditions and their thicknesses had been determined individually using the multiple reflective infrared spectroscopy. It is found that the CuBTA film thickness on the brass increased lineally with increasing the pretreatment temperature. This thickness on 70/30 brass was much thinner than those formed on copper⁹⁾.

Ratios of Zn ions to Cu ions dissolved in the NaCl test solution were in the range of 1.03–3.09. Since the ratio of bulk composition is 0.458, dezincification occurred in the solution. The dezincification was remarkable as increasing pretreatment temperature. The dezincification of the pretreated brass was found to be greater than that of the non-pretreated one. This is probably due to the difference between the inhibitive power of BTA for copper and that for zinc. In other words, BTA produces highly

protective complex films with copper while less protective complex formed with zinc on the brass. Thus, zinc dissolves preferentially in the solution.

3.2 Surface topographies

Typical surface topographies of both the non-pretreated and pretreated brass subsequent to the corrosion test are shown in Fig. 3. Under the scanning electron microscope at magnifications of up to 20000 times, neither significant topographical differences nor any CuBTA crystallites were observed on the 70/30 brass surfaces which had been treated at the temperatures. Severe pitting attack was observed on the non-pretreated brass surface, as seen in Fig. 3-(A). Rows of fine pits in the transgranular area was also characterized for the non-pretreated brass, and the white corrosion products delineated the grain boundaries. Energy dispersive X-ray analysis showed the corrosion products to contain

(A)

(B)

Fig. 3 Scanning electron micrographs of 70/30 brass subsequent to 1 day immersion in 3% NaCl solution of pH 5.9 at 25°C

(A) no pretreatment, (B) pretreated with 0.01 M BTA at 60°C for 5 min. Initial CuBTA film thickness : 37 Å

high Cl and Zn, and minor of Cu.

Figure 3-(B) shows a pretreated brass surface after exposure with relatively smooth areas and pits. The pits formed were rather crystallographic on the surface with 37 Å CuBTA film in this figure. This surface looks similar to BTA-treated copper after the exposure to NaCl solutions⁵⁾. The higher the pretreatment temperature the more unattacked areas were generally observed. It is also found that at the low pretreatment temperatures corrosion attack in the aerated 3% NaCl solutions usually centered on the grain boundaries and the higher temperature films conferred longer lasting protection. Increased temperature probably affects polymerization processes in the CuBTA molecular network. Thus, the higher the pretreatment temperatures, the faster the polymerization, which might build up a CuBTA film with more compact configuration.

3.3 Electrochemical polarization

Typical polarization curves for the 70/30 brass specimens which had been pretreated for 1 minute at temperatures from 25°C to 100°C are shown in Fig. 4. These curves were measured a few minutes after the immersion in aerated 3% NaCl solution of pH 5.8 at 25°C. The anodic Tafel slope of the polarization curves for a non-pretreated and the pretreated brass at 25°C was 25 mV and the pretreated ones at 40, 60, 80 and 100°C maintained almost the same Tafel slopes of 40 mV. The cathodic branch of the curves exhibited much higher polarizations

Fig. 4 Galvanostatic polarization curves of brass in 3% NaCl solution of pH 5.8 at 25°C after 1 min pretreatment at five different temperatures

Table 2 Corrosion current densities and cathodic Tafel slopes obtained from the polarization curves

Pretreatment temperature (°C)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	b_c (mV)
Non-pretreated	1.60	25
25	0.89	58
40	0.56	100
60	0.45	122
80	0.35	173
100	0.30	308

which increased with the pretreatment temperatures. Table 2 represents both the corrosion current densities as obtained from Tafel extrapolation and Tafel slopes of initial part of the cathodic polarization curves. The corrosion current density remarkably decreased with the pretreatment temperature. Also the Tafel slopes for the cathodic curves at the initial polarization increased with the pretreatment temperature. The possible cathodic reaction is mainly an oxygen reduction reaction in the potential range of interest. The electrochemical polarization results indicate the increase of the pretreatment temperature decreases active sites for the oxygen reduction reaction. This facts are in good agreement with the corrosion rate data.

4 Conclusion

The present study indicates that the protective-ness of the CuBTA films formed on 70/30 brass increased with an increase of pretreatment temperature and its period in the aqueous BTA solution. From these results the most desirable protection can be afforded to brass more than 60°C and more 3 minutes of pretreatment in 0.01 M BTA aqueous solution. The electrochemical polarization results show that the inhibition of the pretreated brass is mainly cathodically controlled in the NaCl solution. It appears that the breakdown of the protective films initiates at relatively weak spots of the CuBTA films such as grain boundaries. By the BTA pretreatment surface tarnishing (oxidation) and the grain boundary attack can be reduced greatly. Thus, the pretreatment ensures tarnishing free surface to the brass.

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