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Surface Topography and the Corrosion Prevention of Copper by Benzotriazole

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Abstract

An electron scanning microscopic study was made on the surface topographies subsequent to immersion in 3% NaCl solution in specimens of both fine polycrystalline copper and coarse grained copper with a thin copper-benzotriazolate (CuBTA) film on the surfaces. The results indicate that corrosion initiates at active sites in the protective multilayer films of copper oxide and CuBTA. Protectiveness of the CuBTA films appeared to be related to the crystallographic orientation of the metal substrate and underlying oxide.

Introduction

Benzotriazole (BTA) is one of the most widely used and most effective inhibitors for copper and copper base alloys in various environments. Studies on the nature of its protective films and the mechanisms of their action are still highly controversial in current scientific literature[1)~15)]. Most researchers maintain that a chemisorbed film, about 50 Å in thickness, is formed when copper is dipped into aqueous BTA solution[1)~5),13)]. Poling[6),8)] and Notoya[16)] attribute the protective action of BTA to the formation of a semipermeable Cu-benzotriazolate (CuBTA) polymeric film on the metal surface. This invisible polymeric complex presumably reinforces the copper oxide film normally present on the metal surface. Our previous results[8),16),17)] have shown that typical protective films formed on copper by BTA are better described as multilayers, i. e., $Cu/Cu_2O/Cu^{I}BTA$ (up to 5000 Å). Recently this mechanism has been supported by Paatsch[18)] using photopotential measurements. In near neutral and mildly basic solutions in the presence of BTA, the CuBTA films are usually less than 100 Å in thickness, and appear to exhibit the same surface topography as the underlying air-formed Cu_2O film on the copper. This suggests a relatively uniform multilayer coverage. However, its protectiveness was found to be substantially different among faces of polycrystalline copper. There has been very little work reported on localized attacks of copper with inhibitor films other than of copper oxides[19)]. This paper describes localized corrosion such as pitting, grain boundary attack and preferential dissolution on copper surfaces which were treated with benzotriazole. The relationships between the crystallographic orientation of substrate copper crystal faces and susceptibility to the localized attack were also sought.

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Experimental

Plate of 99.92% OFHC copper (A. D. Mackay. Inc.) was milled to a size of $58 \times 28 \times 2$ mm. A coarse grained copper mirror was prepared by heat treatment of OFHC fine polycrystalline copper under Ar atmosphere at 1010°C for 300 hours. The crystallographic orientation of individual crystal faces of the coarse grained copper was identified by the X-ray Laue-back reflection technique. Surface preparation included mechanical polishing using a 1 μ diamond paste finish, followed by electropolishing in an orthophosphoric acid electrolyte ($H_3PO_4 : H_2O = 1 : 1$ in volume ratio) using a Wenking potentiostat to control the potential of the specimen. Pretreatment of the metal was carried out by immersion in an aqueous solution of 0.02 M benzotriazole at different temperatures for 1 or 5 minutes. The protection afforded to copper mirrors was then exposed to aerated 3% NaCl solutions in the absence of BTA at two pH's of both pH 3.0 and pH 5.9 under a stagnant condition at 25°C.

Topographies of copper mirror specimen surfaces were examined using an ETEC Autoscan U-1 scanning electron microscope. To gain information on the chemical composition of the corrosion products formed on the copper surface, an Ortec 5200 energy dispersive X-ray analyser in conjunction with the scanning electron microscope was applied. Infrared spectra of CuBTA films formed on copper were recorded on a Perkin-Elmer Model 521 infrared spectrophotometer by means of multiple reflectance optics. The thickness of inhibitor film on the metal mirror was estimated using 9 reflections at 70° incidence to record reflection-absorption spectra[6].

Results and Discussion

Pretreated surfaces prior to immersion in an corrosive environment were structureless under the scanning electron microscope at a magnification of about 20000. However, these same surfaces, after a 1 day immersion in neutral chloride solution in the absence of inhibitor, showed that pitting corrosion and grain boundary attack predominated. In addition, after immersion in a weakly acidic NaCl solution preferential dissolution was observed on the pretreated copper surfaces of both fine polycrystalline copper and coarse grained copper, where protective surface films disappeared and the surfaces were roughened in some of the grains while other grains remained showing no evidence of attack.

Figure 1 shows a typical pitting corrosion on the pretreated copper mirror surfaces after a 1 day immersion in an aerated 3% NaCl solution of pH 5.9 at 25°C. Generally the CuBTA film thickness formed in neutral aqueous solution of BTA increased with both increasing pretreatment period and temperature[20]. In this specimen the initial "average" CuBTA film thickness was 48 Å for the pretreatment temperature at 60°C with a period of 5 mins. The "average" film thickness indicates the average of the thicknesses of the film at 9 different areas on the copper surface. Pits were observed both at grain boundaries and on crystal faces of fine grained copper surfaces. Pitting attack was confined to certain face where pit density is particularly higher than in neighboring faces. Unattacked areas were relatively smooth as shown in Figure 1-(B). In other words neither significant topographical differences

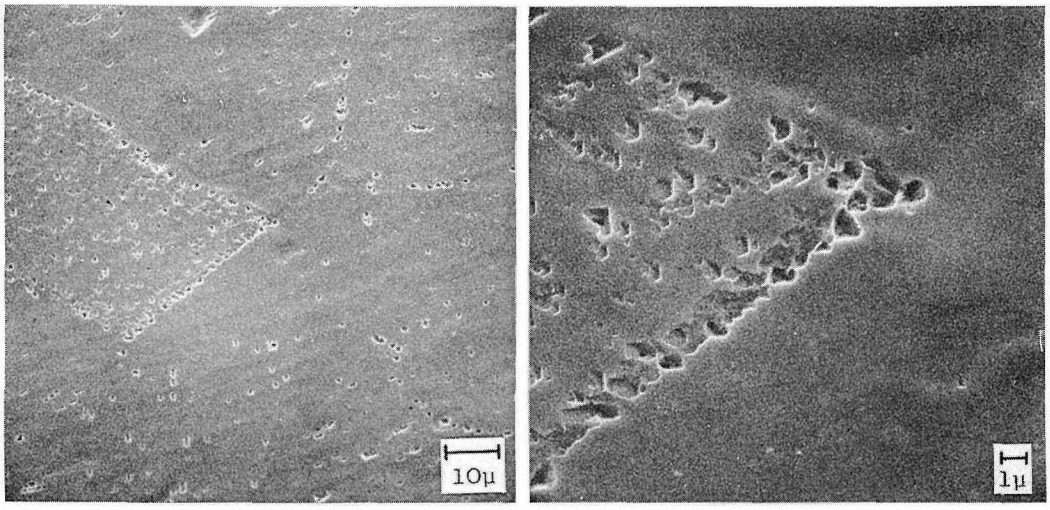


Figure. 1. Pitting attack of pretreated copper mirror after 1 day exposure to aerated 3% NaCl of pH 5.9 at 25C°. (A) is a special area in (B). Pretreatment temperature: 60°C, its period: 5 mins.

nor any CuBTA crystallites were observed on the copper surfaces except for the presence of pits. These areas are assumed to be still covered with protective inhibitor films. The CuBTA films appear to have grown eqitaxially on top of the air-formed Cu_2O,[8] or at defects in the Cu_2O film, and are protective, particularly when repair is maintained by the continuing presence of BTA in a corrosive environment. The susceptibility to intercrystalline pitting corrosion in the neutral NaCl solution would depend on the protectiveness of the duplex Cu_2O/CuBTA pretreatment films. The CuBTA film formed on defective Cu_2O would be less protective than that on less defective Cu_2O which has ionic as well as electronic resistance[21]. The defects present in the underlying Cu_2O were caused by the lattice disregistry of copper oxide at the substrate copper during oxidation[22]. The scanning electron micrographs indicate that pitting corrosion initiates at the defects or at active sites present in either underlying Cu_2O or CuBTA films.

Figure 2 shows grain boundary attack observed on copper mirror which was previously treated with the BTA solution at 25°C for 5 mins. followed by exposure to a 3% NaCl solution of pH 5.8 for 1 day. Pits and grain boundary attack produced on the pretreated copper surfaces were crystallographic in many cases. Figure 2-(B) illustrates a higher magnification of the selected area of the same specimen shown in Figure 2-(A). The shape of the pits at grain boundaries was dependent on the relative orientation of the substrate grains and were independent of the pretreatment temperature or CuBTA film thickness. A secondary pit is seen at the bottom of a pit at the lower-left position in Figure 2-(B). The secondary pit seems to undermine and to enlarge the pit along the grain boundary. This type of attack is preferably observed on the surfaces covered with a relatively thin CuBTA films. Although grain boundary attack is generally determined by impurities present at grain

boundaries, an increase in the difference in neighboring crystal orientation also increases the favoring of the attack, because lattice discontinuities will increase with increasing difference in orientation among neighboring grains.

A preferential dissolution was observed on the mirror surfaces after a 1 day immersion in a weakly acidic NaCl solution, as shown in Figure 3. In this case the

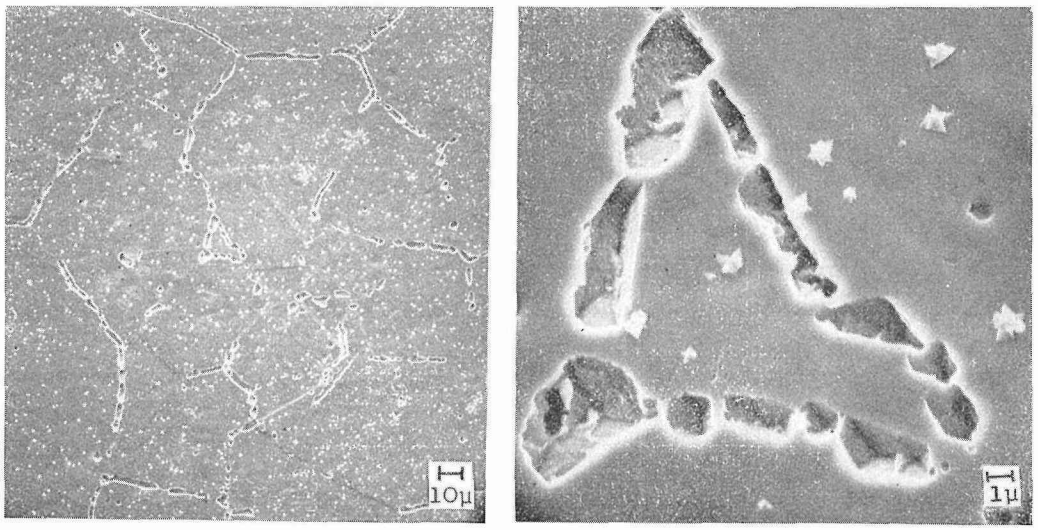


Figure. 2. SEM's of Cu surfaces after 1 day exposure to aerated 3% NaCl of pH 5.8. Before the exposure Cu mirror was pretreated with 0.02 M BTA for 5 mins. at 25°C. (A) 400 × (B) 4000 ×.

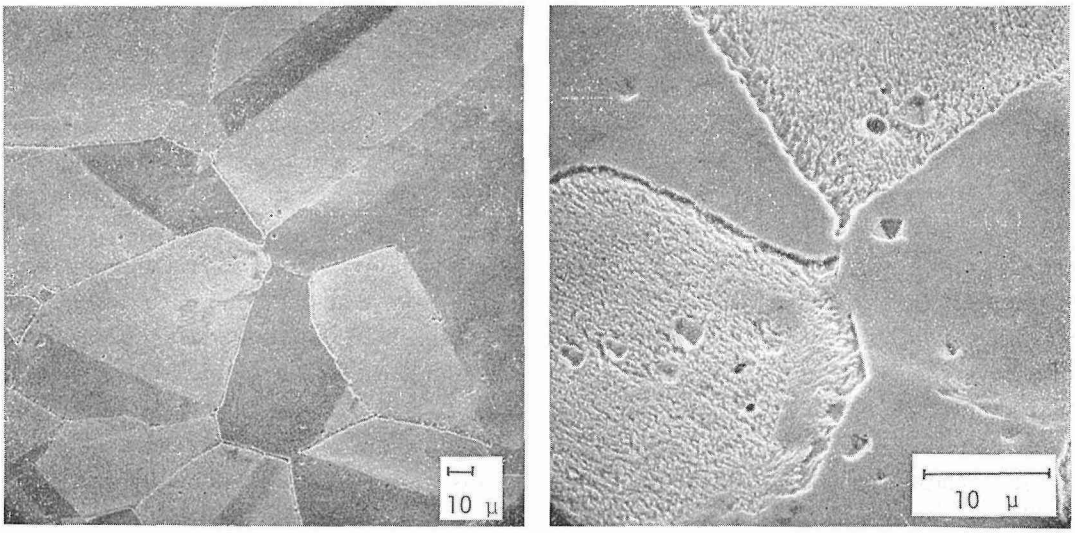
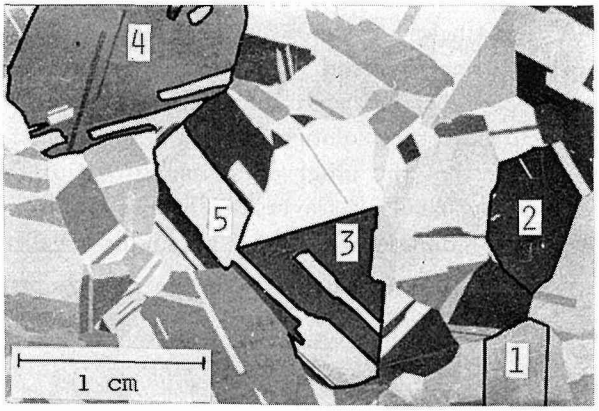
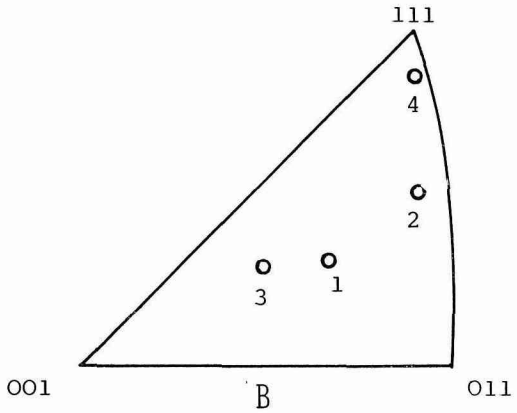


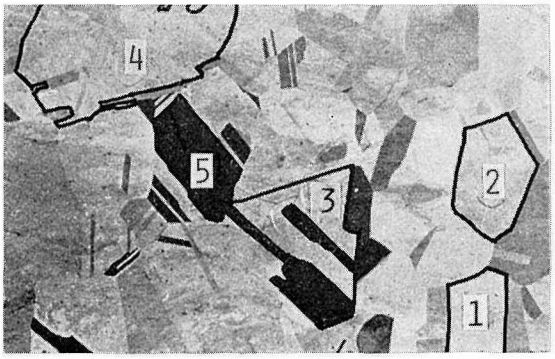
Figure. 3. Preferential attack of pretreated Cu mirrors after 1 day exposure to aerated 3% NaCl of pH 3.0 at 25°C. Pretreatment temperature: 25°C. (A) 400 × (B) 2000 ×.



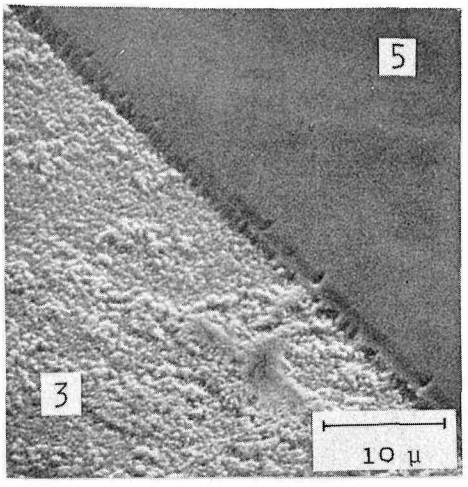
A



B



C



D

Figure. 4. A. Coarse grained copper specimen metallographically etched in nitric acid. B. diagram showing locations of the selected crystal faces in the stereotriangle. C. Surface appearance of the pretreated copper specimen after 51 hours exposure to 3% NaCl solution of pH 3.0 at 25°C. Pretreatment was conducted in 0.02 M BTA at 60°C for 5 mins. D. Scanning electron micrograph of both attacked (No. 3) and unattacked No. 5) areas.

initial average CuBTA film thickness was 63 Å. Some of the crystal faces are relatively smooth while others are roughened. This type of corrosion was only observed when the pretreated copper surfaces were immersed in uninhibited-acidic chloride solutions. On exposure to corrosive solutions of pH less than 3.5 where the copper oxide is unstable, it is likely that the observed stripping of CuBTA films was caused by dissolution of the unstable Cu_2O interlayers. The preferential dissolution also appears to be an intermediate condition between the highly localized attack of either

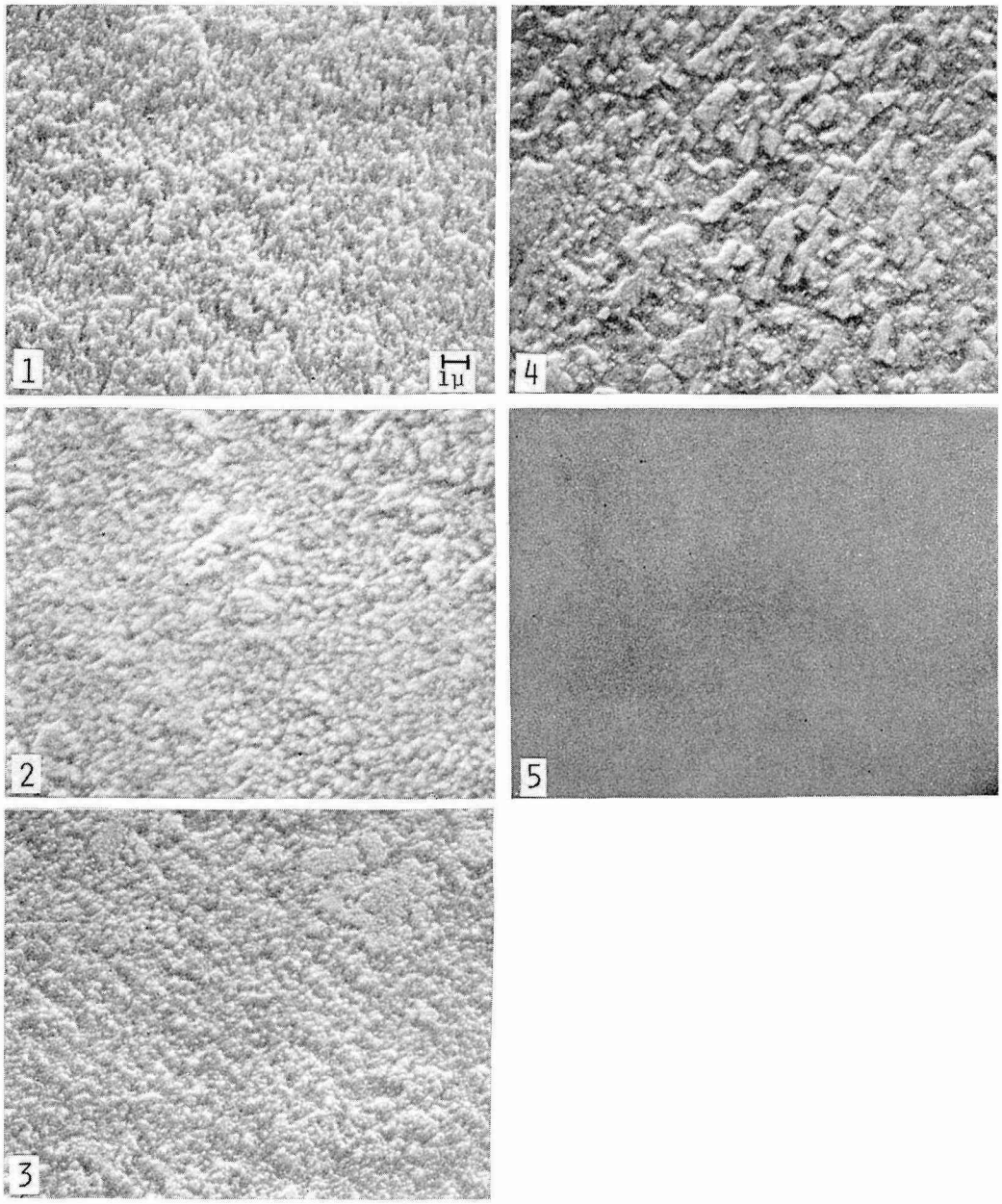


Figure. 5. Surface topographies of the selected crystal faces in a diagram of Figure. 4-(C) Magnification: 4000 ×.

pitting corrosion or grain boundary attack and uniform corrosion.

A preferential dissolution was also observed on pretreated copper surfaces of coarse grained copper. This attack was reproducible in the same specimens. In Figure 4 the top photograph shows the coarse grained copper specimen metallographically etched in nitric acid. Crystallographic orientations of the four selected crystal faces were determined, and are found to be located in a stereotriangle (B). The No. 5 crystal orientation is not shown in the diagram. Figure 5-(C) shows the preferential dissolution of pretreated copper. Most of the crystals were attacked and are shown in white, while grain No. 5 was unattacked and remained specularly reflecting. The Cu_2O interlayers should be unstable during the exposure at pH 3.0. It is interesting to note that even at this pH the CuBTA film still remains on the surface after a 15 hours exposure. This contradicts the results of Ferrari et al[23], who described the CuBTA film as being removed easily by wetting with a salt solution. A grain boundary between the crystal faces of No. 5 and No. 3 is illustrated in the Figure 5-(D). Surface appearance of the selected faces including both No. 3 (rough) and No. 5 (smooth) are also presented in Figure 5. A relatively unattacked structure was observed on No. 4 grain surface which is adjacent to the (111) face. The (111) face is the most closely-packed face in copper. No. 1 face, having higher index, shows fine structure while both No. 2 and No. 3 faces show an intermediate roughness. Although the roughness of the attacked surfaces of No. 1 through No. 4 are different, no significant difference in chemical composition among the individual corroded surfaces could be detected using the X-ray dispersive analysis. Thus, further studies to identify atomic elements and to compare the differences in their concentration on the different crystal faces are being contemplated.

Conclusion

Surface topographies of pretreated copper subsequent to immersion tests were demonstrated in scanning electron micrographs. It was concluded that perferential dissolution of pretreated copper occurs on preferred crystallographic planes in weakly acidic chloride solutions. It appears that in the thin CuBTA film, some structural difference is expected among the CuBTA films formed on copper under different conditions in relation to crystallographic orientation of the metal substrate and underlying oxides. This structural difference determines the protectiveness of the inhibitor films. Corrosion of BTA-treated copper initiates at defects in the protective films which are pathways of easy diffusion for copper ions. The remaining CuBTA films on the surfaces, after immersion, prevent surface stains or tarnishing, even though the copper surface are subjected to localized attack at grain boundaries.

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