Corrosion Protection of Copper by Conductive Polypyrrole Films Incorporated with Inhibitors

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Copper and its alloys were widely used as structural materials, because the resistivity of copper against corrosion is relatively high. When one uses copper at seashore or in seawater, however, the corrosion damage is much increased and surface finishing for enhancement of corrosion resistivity is thus required. In this study, the new anti-corrosion technique has been developed by a conducting polymer (CP) coating using polypyrrole (PPy) film. For the stable anti-corrosive surface finishing, a self-healing property should be incorporated in the surface coating. For the self-healing property, the PPy film have been doped with corrosion inhibitors of copper, for which Phytic acid (C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}P\textsubscript{6}, IP\textsubscript{6} or Phy) and benzotriazole (BTA) have been adopted in this study.

In chapter I, previous studies of conducting polymers (CPs) were reviewed, in which the origin of conductivity, doping of ions into CPs, synthesis method, mechanism of electropolymerization of conducting polypyrrole (PPy) were introduced. The previous studies on the protection of copper against corrosion by CP film were summarized. The present issues on the corrosion protection of copper and its alloys were surveyed and the aim of this work was described.

In chapter II, The PPy was electrochemically prepared on copper in phytate solution. Phytate compounds existing in various plants have been assumed to be one of environmentally friendly inhibitors of copper. The PPy film thus formed was doped with phytate ions simultaneously with the polymerization-deposition. The open circuit potential in NaCl solution of the copper covered with the PPy-IP\textsubscript{6} was maintained in a high potential state for the period longer than 800 h
and the dissolution of copper was decreased to 1/19 relative to bare copper.

In chapter III, we discussed the effects of the solution pH and applied CD on the PPy polymerization-deposition process on copper electrode as well as on the protection property of the PPy film. The oxidation degree of the PPy film depended on the solution pH for preparation, increasing with the more acidic solution. In the more acidic solution, the higher CD is required to form the PPy layer. When one oxidized bare copper in phytic acid solution at various pHs containing pyrrole monomer, a thin layer consisting of complex compound of Cu-IP₆ was firstly formed, followed by the formation of the PPy layer doped with IP₆ on the complex compound layer. The complex compound layer passivated the copper surface and its thickness increased with the lower pH value of the solution and the lower CD applied. Protective property of the PPy films also depended on the solution pH. It was found that the PPy coating prepared in the IP₆ solution at pH 4 exhibited the most protective property against copper corrosion.

In chapter IV, the protection mechanism was examined for the PPy by using electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopy (EIS). Two different PPy coatings were coated on copper from phytic acid and sodium di-hydrogen phosphate solution. The PPy film doped with Phytate anions (PPy-Phy⁻) was found to work as a cationic perm-selective membrane and to effectively inhibit penetration of chloride ions to the PPy film. The copper covered with PPy-Phy⁻ was thus maintained in passive state for the longer period than 2 months and the dissolution of the copper were inhibited by 1/100 relative to that of bare copper. The copper covered with PPy-H₂PO₄⁻ film prepared in sodium di-hydrogen phosphate solution possessed an anionic perm-selectivity and the dissolution of copper was inhibited by 1/13. The degradation of the PPy films was examined by EIS and EQCM during the immersion in the NaCl solution. The effective protection of PPy-IP₆ film was assumed due to inhibition of penetration of Cl⁻ ions from NaCl solution.

In chapter V, benzotriazole (BTA) was added to the solution for Polypyrrole (PPy) deposition in oxalic acid solution. A homogenous PPy film was anodically formed on a copper electrode by constant current control in an oxalic acid aqueous solution containing Py monomer and BTA. Effect of the BTA addition on the PPy formation and on its corrosion property was investigated with different methods by comparing to the control samples. The addition of BTA to the oxalic acid solution facilitated the formation of the PPy film on the copper substrate and enhanced the adhesive
strength of the PPy film on the copper. The PPy film prepared in the oxalic acid solution containing BTA (PPy-Ox-BTA film) effectively protected copper against corrosion in 3.5 wt. % NaCl solution. After 400 h immersion, dissolution of copper covered with PPy-Ox-BTA was decreased to 20% relative to that of bare copper. The protective property may be assumed to be caused by the presence of BTA on the copper surface and in the PPy film. The self-healing property of the PPy film was also greatly improved due to the addition of BTA during PPy formation.

In this work a new anti-corrosive coating of copper at seashore or in seawater was developed. The conducting PPy coatings doped with corrosion inhibitors of Phytate and BTA were prepared on copper and the coatings formed effectively inhibited corrosion of copper.