Post-treatment of Tinplate by Cathodic Electrolysis in Molybdate Solutions

N. Tagami[1], M. Morimitsu[2] and M. Matsunaga[1]

[1]*Department of Applied Science for Integrated System Eng., Kyushu Institute of Technology Tobata, Kitakyushu, 804-8550, JAPAN*

[2]*Department of Environmental Systems Science, Doshisha University Kyo-tanabe, Kyoto, 610-0321, JAPAN*

Tinplate can offer corrosion protection of iron in organic acid solutions. This corrosion protection is, however, weakened when the solution contains nitrate ions and dissolved oxygen gas. The latter case sometimes induces a serious problem that an abnormal corrosion of tinplate occurs by the reduction of oxygen. In this study, we tried to develop a novel post-treatment process to suppress the oxygen reduction in organic acid solution containing oxygen gas so as to inhibit the anomalous corrosion of tinplate.

Tinplate specimens (10 mm x 15 mm) used in this study were prepared by electroplating of tin on steel in Ferrostan bath. The post-treatment of the specimen was carried out by cathodic electrolysis in the aqueous solution containing 0.1 mol/dm^3 potassium molybdate and 0.1 mol/dm^3 trilithium citrate at room temperature. Electrochemical measurements were performed using the organic acid solution containing 3.35 g/dm^3 citric acid, 3.45 g/dm^3 trisodium citrate, 1.2 g/dm^3 DL-malic acid, and 200 g/dm^3 sucrose (pH 3.7) at 293 K. The concentration of oxygen dissolved in the solution was kept to be 35 ppm. Linear sweep voltammograms at 1 mV/s were recorded to determine corrosion current density and corrosion potential following a usual manner. The surfaces of the specimen before and after the post-treatment were characterized by XPS, SEM, and EPMA.

The cathodic electrolysis of tinplate specimen was carried out at various potentials for 60 min., and then the polarization curve of the specimen after the post-treatment was measured. The corrosion current densities obtained from the polarization curves are shown Fig. 1. It can be seen that the post-treatment can reduce the corrosion current density of tinplate in the solution containing oxygen gas when the electrolysis potential is lower than -1 V. Especially, when the post-treatment carried out at -1.20 V, the corrosion current density decreased about 15 % comparing with the specimen without the post-treatment. The comparison of the polarization curves with and without the cathodic electrolysis also indicated that the decrease in corrosion current density was caused by the suppression of oxygen reduction. The effects of the electrolysis period on the corrosion current density were also investigated. As shown in Fig. 2, the corrosion current density became lower with increasing electrolysis period and reached to a constant value when the electrolysis period was 20 min. or more.

The decrease in corrosion current density and the suppressed reduction of oxygen gas was caused by the modification of the tinplate surface by the cathodic electrolysis. XPS analysis of the modified tinplate surface revealed that the outermost surface contained Mo(VI) and Mo(III) compounds, which seems to play a role as a protection layer to avoid oxygen reduction. The nature of the protection layer and the detailed mechanism to suppress oxygen reduction will be also discussed.

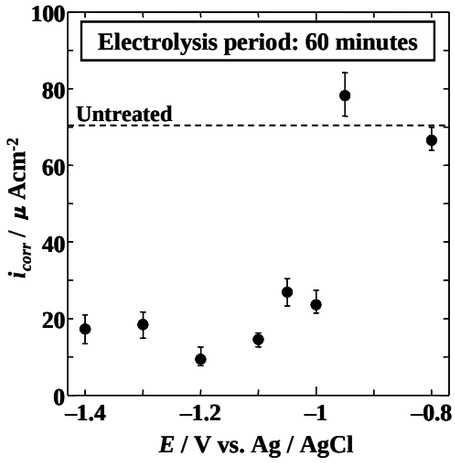

Fig. 1 Effects of the electrolysis potential on the corrosion current density.

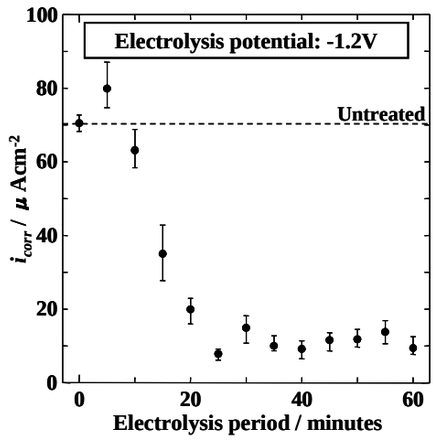

Fig. 2 Effects of the electrolysis period on the corrosion current density.