

Corrosion Behavior of Electroplated Tin/Zinc Deposits

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Electroplated Sn-Zn deposits have been proposed as a replacement of the widely used cadmium coatings. Experiments have shown that Sn-Zn coatings have both the barrier property of Sn and the sacrificial property of Zn. At open circuit potential, Zn dissolution is the only corrosion reaction.

The electrochemical quartz crystal microbalance (EQCM) was used together with traditional electrochemical techniques in order to obtain the plating efficiency and the corrosion rate of tin/zinc deposits¹. When deposition occurs from an unstirred solution, hydrogen evolution leads to a pH change in front of the electrode and after some deposition time to the formation of a hydroxide layer on top of the deposit². This can be avoided by bubbling nitrogen through the solution during plating.

Fig. 1 shows the voltammetric curve for a sample with 70% tin, together with those of pure zinc, pure tin, and of the steel substrate. Scan rate was 1mV/s. In the potential range below -500mV the current remains rather small, but is sufficient for the complete oxidation of the zinc content of the sample. This was demonstrated by scanning electron micrographs.

Samples that were deposited onto the gold layer of an EQCM were transferred into a corrosive solution, in our case 0.1 M sodium sulfate + sulfuric acid, pH = 3.6. Here the corrosion rate is constant over extended periods of time and corresponds to a zinc dissolution current of a few microamps per square centimeter.

The open circuit potential of a freshly prepared tin/zinc deposit is very close to that of pure zinc in the same solution. However, during corrosion the open circuit potential becomes more positive with time. This effect is more pronounced with higher tin content in the deposit, as is shown in Fig. 2.

There is virtually no mutual solubility of tin and zinc at room temperature. The deposits, therefore, consist of pure tin and zinc crystals. The distribution of these crystals is so fine that it cannot be resolved by EDX analysis. It seems that the zinc crystals are located

between the larger tin crystals. During the preferential oxidation of zinc during the corrosion period pits and crevices must be formed between the remaining tin crystals. The cathodic reaction, hydrogen evolution, occurs at the whole outer surface. Hence, when pits and crevices are formed, there must be an IR drop because of the spatial separation of the anodic and cathodic sites. This IR drop leads to the observed increase of the open circuit potential. It should also lead to a continuous decrease of the anodic current and therefore to an increase in the lifetime of the protective action of the deposit. This model will be tested by in-situ corrosion rate determination and by electrochemical impedance spectroscopy.

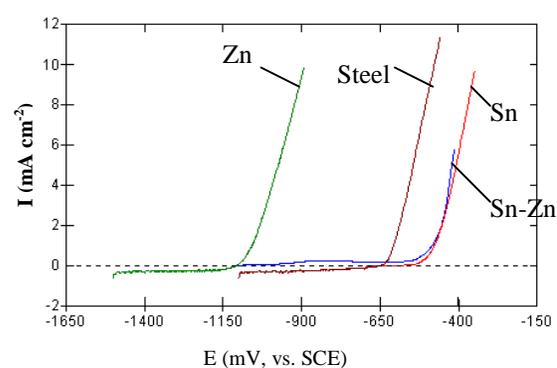


Fig. 1. Polarization curves of Sn, Zn, steel substrate and Sn-Zn alloy deposit in 0.1M Na₂SO₄ Solution (scan rate: 1 mV/s)

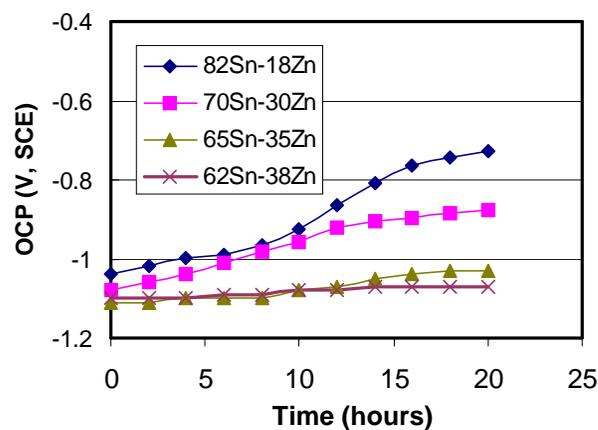


Fig. 2. Open circuit potential changes with time for Sn-Zn deposits with different compositions in 0.1M Na₂SO₄ solution

¹ C. Eickes, J. Rosenmund, S. Wasle, K. Doblhofer, K. Wang, K.G. Weil, *Electrochimica Acta* 45 (2000) 3623-3628.

² K. Wang, H. W. Pickering, K.G. Weil, *Electrochimica Acta*, in press.