Corrosion of Lead Plated Titanium in Sulfuric Acid

Jinxiang Dai, Zongtao Zhang, T. Danny Xiao, David Reisner, US Nanocorp, Inc., 74 Batterson Park Road, Farmington, CT 06032

Introduction

Lead acid batteries are well developed and have been used for over 100 years. Advanced lead acid batteries with high energy density are pursued. To reduce the overall weight of the lead acid batteries, lead plated titanium substrates have been developed to substitute lead alloy grids [1]. To use titanium grid, one of the most important issues is to solve corrosion problems in sulfuric acid electrolyte. In this research, the corrosion of a lead plated titanium foil with titanium nitride interlayer has been studied in a 30% wt sulfuric acid solution at 49°C.

A titanium foil was electroplated with lead to give the same electrochemical characteristics as pure lead [1]. A Ti_xN interlayer was formed to improve bonding strength between Pb and Ti as well as corrosion resistance (Fig.1.)

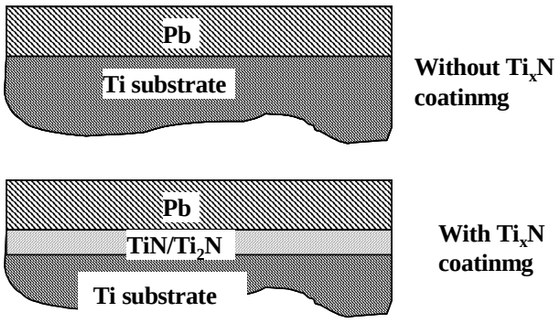

Fig.1. Schematic illustration of the coatings on the titanium substrate

Titanium nitridation: The titanium nitride coating was produced by surface nitridation at an elevated temperature in a nitrogen atmosphere. The likely reactions are:

$$2Ti + N_2 \rightarrow 2TiN \quad (1)$$
$$4Ti + N_2 \rightarrow 2Ti_2N \quad (2)$$

The TiN and TiN_2 was identified by x-ray diffraction (XRD). The thickness of the Ti_xN was measured by an intersection SEM observation. At 900°C, the thickness of the formed Ti_xN interlayer increases with reaction time, but the reaction rate decreases with time because the produced Ti_xN resists further reaction (Fig.2.).

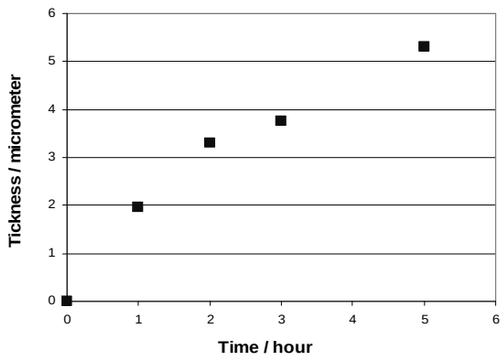

Fig.2. Thickness of Ti_xN at different reaction time

Electroplated lead coating: Lead coating was produced by electroplating in a solution containing $Pb(OSO_2CH_3)_2$ and methane sulfonic acid (MSA). The composition of the electroplating solution and electroplating parameters are listed in Table 1.

Table 1. Bath composition and electroplating parameters

Constituent	Amount (g/L)
Lead as metal	80
MSA concentration	120
NF2540 additive	60-120
Temperature	16-30°C
Current density	0.8-4 A/dm^2
Stir	Mechanical grade 3-8

Note: NF 2540 from OMG

Corrosion: The corrosion resistances of titanium foil with different coatings were evaluated by weight changes after immersing in a 30% wt H_2SO_4 at 49°C. The weights of samples were measured at different durations. For comparison, pure lead was also tested and the results are illustrated in Fig.3.

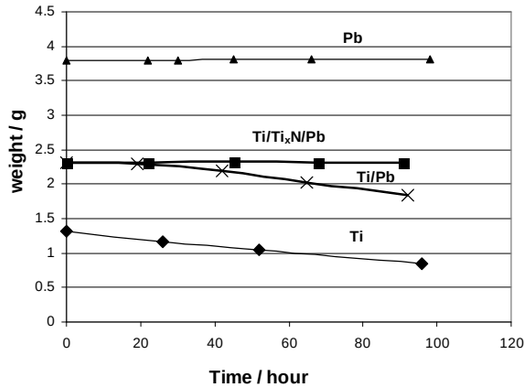

Fig.3. Weight change vs time for titanium foil with different coatings in 30% wt H_2SO_4 solution. Ti_xN thicknes : 5μm; Pb thickness: 15μm; 49°C.

The pure lead foil and the titanium foil with Ti_xN/Pb 2 layer coatings have no weight change in 100 hours. The titanium foil without any coating have highest corrosion rate. The titanium with Pb coating have lower corrosion rate compared with pure Ti in 40 hrs and have similar corrosion rate after 40 hrs. Initial dissolve of titanium will destroy the Pb coating on Ti foil and titanium loses protection and becomes the same as pure Ti without any coating.

Conclusion

The thin layer of Ti_xN formed by nitridation of the titanium in N_2 at high temperature has good corrosion resistance to sulfuric acid at elevated temperatures. The lead coating can be formed on the surface of Ti_xN interlayer via electroplating. The composite coating makes titanium have both corrosion resistance and the same electrochemical characteristics as pure lead. The titanium grids with composite coatings are likely used as grids for light weight lead acid batteries.

Reference

1. J.Dai, Z.Zhang, T.D.Xiao, D.E.Reisner, "Lead Plated Titanium Grids for Lead Acid Batteries", to be presented, 41st Power Sources Conference, Philadelphia, PA, June 14-17, 2004