

Effect of process conditions on the characteristics of sol gel TiO₂ dip coating

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1. Introduction

Morphology (structural shape including surface homogeneity, thickness, cracking, and porosity) is of crucial importance in corrosion barriers and in photo-electric, photo-catalytic, and optical applications of dip coated sol-gel TiO₂ film. Coating homogeneity affects the properties and quality of the coating [1]. Inhomogeneous coating can weaken the local chemical barrier properties of a coating and induce substrate corrosion. Inhomogeneity of a coating surface can induce uncertainty in measurements of optical properties. Inhomogeneous coating thickness can make it difficult to control the photo-electric and photo-catalytic properties.

In this study, the effects of the process conditions (withdrawal rate, coating repetition) on the morphological characteristics of sol gel TiO₂ film during dip coating were investigated.

2. Experimental details

We carried out dip coating experiments to observe the effect of the withdrawal rate, coating repetition, and heat treatment on morphological development (homogeneity, thickness, defects) in coated film. Sol was prepared with acetic acid catalyst and EAcAc (EthylAcetoAcetate) chelating agent. Withdrawal rate varied between 0.4 mm/sec and 3.2 mm/sec. Multilayered coatings were prepared by conducting 1, 2, 3, 5, and 10 cycles of coating. Heat treatment was carried out for 30 minutes at 450°C in air. The properties of the TiO₂ film were characterized by visual observation, SEM, FIB, FTIR, and EIS (Electrochemical Impedance Spectroscopy).

3. Results and discussion

3.1 Coating surface morphology

Morphological variation for the 3 times coating specimens at withdrawal rate varying between 0.4 mm/sec ~ 3.2 mm/sec is shown in Fig. 1.

The thickness inhomogeneity increased as the withdrawal rate and the number of coating cycles increased. The specimen with withdrawal rate of 0.4 mm/sec had the smallest lateral area, the least cracking, and the best homogeneity as shown in Fig. 1. The neck area was also much reduced compared to that of the other high withdrawal rate specimen.

The size of the bottom homogeneous area tended to increase as the withdrawal rate decreased. As the withdrawal rate increased, the bottom and central homogeneous areas decreased, and cracking increased in the lateral area.

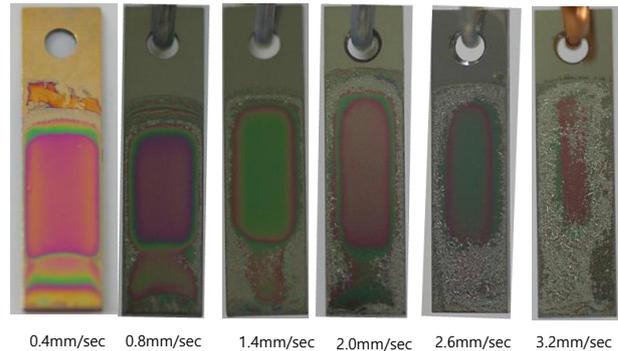


Fig. 1 Morphological variation with withdrawal rate (0.4 mm/sec ~ 3.2 mm/sec), dip coating (3 times, after drying).

Sol-gel film grows by formation of a solid network at the contact line, which is the front interface between sol and air on the specimen surface. Two processes compete to feed sol to the contact line. One is capillary feeding; the other is viscous drag [2]. The process that controls feeding is determined by the withdrawal rate. Capillary feeding is the controlling process for withdrawal rates below 0.1 mm/sec, while viscous drag is the controlling process for withdrawal rates above 1 mm/sec. There is an intermediate regime at withdrawal rates of 0.1mm/sec~1mm/sec [2].

3.2 Coating thickness

Data measured in this study (using FIB and reflectance) for thickness of sol-gel dip coated TiO₂ as a function of withdrawal rate are displayed in Fig. 2.

There is some uncertainty in the thickness values from the different coating process conditions and measurement methods. All thickness data are displayed in the same plot in Fig. 2. The average value of the thickness is plotted on the graph for coatings of several cycles; the thickness data for specimens after heat treatment are also displayed in the same graph. Data obtained using FIB and reflectance method are marked separately in the graph. Fig. 2 suggests that the thickness generally increases as the withdrawal rate increases.

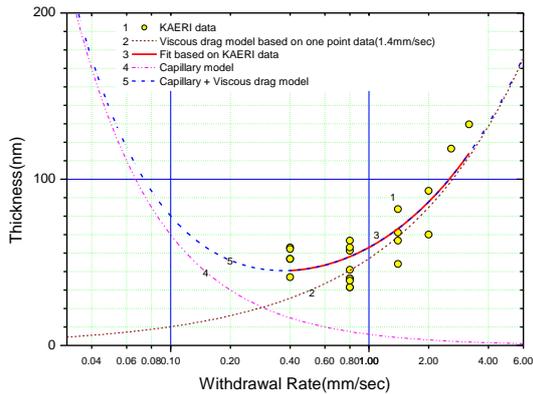


Fig. 2 Thickness as function of withdrawal rate.

The thickness (t) of a sol-gel film grows with sol feeding by capillary action or by viscous drag, according to the equation below [2].

$$t = C_1 u^{1/2} + C_2 u^{2/3} \quad (1)$$

$$C_1 = \frac{cME_0}{\alpha\rho L}, \quad C_2 = 0.94 \left(\frac{\gamma}{\rho g}\right)^{1/2} \left(\frac{\eta}{\gamma}\right)^{2/3}$$

where C (mol L⁻¹) is the inorganic molar concentration of the solution, M (g mol⁻¹) is the molar weight, E_0 (m³s⁻¹) is the rate of solvent evaporation, α is the volume fraction of inorganic solid material, ρ (kg m⁻³) is the density of inorganic solid material, γ (N m⁻¹) is the surface tension, g (m s⁻²) is the gravitational acceleration, and η (Pa s) is the viscosity. The first term in Equation (1) is the contribution by capillary feeding. The second term in Equation (2) is the contribution by viscous drag, which was suggested originally by Landau and Levich [3].

To approximately determine the constants (C_1, C_2), calculation was carried out as below:

C_2 was calculated and found to be $5.233 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ by substituting the measured thickness values of 65.5 nm (the average value of 4 points) at the withdrawal rate (u) of 1.4 mm/sec into Equation (1). In this calculation, the first term of Equation (1) can be neglected because the contribution of capillary feeding is negligible at this withdrawal rate. Equation (1) can be written as

$$t = C_1 u^{1/2} + 5.233 \times 10^{-6} u^{2/3} \quad (2)$$

By using Equation (2) to fit the thickness data (KAERI), C_1 was calculated and found to be $6.661 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. From these results, the thickness of the oxide film (t) can be expressed as

$$t = 6.661 \times 10^{-12} u^{1/2} + 5.233 \times 10^{-6} u^{2/3} \quad (3)$$

This equation is shown as curve #5 in Fig. 2. This is an approximation, and experimental data will be needed

to confirm the model, especially in the regime of the capillary model ($u < 0.1$ mm/sec). Direct measurement of thickness is quite rare so it is meaningful to set up a relation using convincing thickness values obtained by SEM and FIB. With some elaboration, good control of thickness is possible using this semi experimental model, which is needed as a further study.

4. Conclusions

The effects of the process conditions (withdrawal rate, coating repetition, and heat treatment) on the morphological development of sol gel dip coating were investigated to obtain an understanding of the controlling variables of TiO₂ coating.

1) By controlling the withdrawal rate in the intermediate regime of viscous drag and capillary feeding, we were able to minimize the 'edge effect' and fabricate a homogeneous (thickness) coating.

2) The thickness of the coating is dependent on the withdrawal rate. By controlling the withdrawal rate, it is possible to control the thickness of the dip coating. With a withdrawal rate between 0.4 mm/sec and 0.8 mm/sec (intermediate regime of viscous drag and capillary feeding), the TiO₂ thickness was about 40 nm. We proposed an equation for the thickness of sol-gel film as a function of the withdrawal rate. This semi experimental model makes possible good control of thickness, although it will require some elaboration of the equation via further experimental data

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