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Effect of a High Magnetic Field on the Electrodeposition of Tl_2O_3 Films

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1 INTRODUCTION

The surface condition of metal or metal oxide films determines the effectiveness of some properties, especially catalytic properties. Therefore, much attention has been paid to developing techniques for surface control. According to Dash and King¹⁾, the surface morphology of the electrodeposition of copper was influenced by magnetic fields. Fahidy²⁾ studied the effects of magnetic fields on electrochemical processes, in particular, the magnetohydrodynamic (MHD) effect, and indicated the usefulness of magneto-electrolysis. There have been only a few papers reporting clear changes in either surface morphology or crystal orientation in magneto-electrolysis.

One of the most drastic magnetic field effects on crystal morphology was observed in the growth of silver metal leaves from an aqueous solution³⁾. The growth morphology showed a fractal pattern without a magnetic field, and a dense radial pattern with a field of 8T. One possible explanation proposed for this phenomenon is the MHD effect on the diffusion of the silver ions.

This paper deals with the electrodeposition of thallium(III) oxide on titanium substrate in very high magnetic fields of up to 14T. Switzer⁴⁾ reported that the Tl_2O_3 film deposited at a potential giving kinetic-controlled current consisted of a dense aggregate of columnar single crystals. It is expected that the morphological change of such a film is caused by the MHD effect on not only the

mass-transfer process of an electrode-active material, but also the interface kinetic process in the mechanism of crystal growth.

2 EXPERIMENTAL

2.1 Preparation of Tl_2O_3 films

All chemicals were of guaranteed reagent grade. The films of Tl_2O_3 (approx. $15\mu m \times 2cm^2$) were electrodeposited on a Ti substrate at +0.5V vs. SCE as described⁴⁾. The electrodeposition was carried out in a $0.5mol\ dm^{-3}$ CH_3COOTl - $1.0mol\ dm^{-3}$ $NaOH$ aqueous solution at 25°C under nitrogen atmosphere using a Bioanalytical System Model 100B electrochemical analyzer. The electrochemical cell consisted of a pre-treated Ti plate working electrode⁵⁾, a Pt wire counter electrode, and a saturated calomel electrode. The films were rinsed with distilled water and acetone, followed by air-drying at room temperature for approx. 3h and then drying over silica gel.

2.2 Generation of magnetic fields

The experiments with high magnetic fields were performed at the High Field Laboratory of Tohoku University. Magnetic fields were generated by a Bitter magnet with a maximum field of 15T in an 82mm bore at room temperature. The applied magnetic field was parallel to the Ti plate electrode and perpendicular to the faradaic current.

2.3 Analytical procedures

Voltammetric measurements were carried out using the same electrochemical methods as described in 2.1. The working electrode was a Ti plate with approx. $4mm^2$ of surface area. SEM observation was made on a Hitachi HHS-2R. X-ray diffraction patterns were measured with a Rigaku RAD-B using $CuK\alpha$ radiation.

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Fig. 1 Linear sweep voltammogram of 0.1 mol dm^{-3} CH_3COOTl in 1.0 mol dm^{-3} $\text{NaOH-H}_2\text{O}$.

3 RESULTS AND DISCUSSION

It is known that the anodic oxidation of Ti increases its resistance to corrosion. Metikos-Hukovic and Ceraj-Ceric⁵⁾ examined the mechanism of non-stoichiometric oxide formation in the anodic oxidation of Ti. The coating of highly conductive Ti_2O_3 onto Ti prevented the anodic oxidation of the substrate and enabled it to function as a working electrode at positive potentials in an alkali solution.⁴⁾ The linear sweep voltammogram of 0.1 mol dm^{-3} CH_3COOTl is given in Fig. 1. The concentration of 0.1 mol dm^{-3} was selected to be close to the initial concentration (0.5 mol dm^{-3}) for the electrodeposition of Ti_2O_3 , though the former was unusually high for voltammetric measurements. Obara and Sekine⁶⁾ studied the anodic oxidation of Ti(I) to Ti_2O_3 in neutral and alkaline solutions using the polarographic and potential sweep methods with platinum microelectrodes. The over-all reaction in the pH range 11–14 was determined as follows⁶⁾:

Using the X-ray diffraction patterns and SEM images, we confirmed that the films grown on Ti consisted of highly oriented columnar Ti_2O_3 , both when they were grown without any magnetic field as earlier described⁷⁾, and with a strong magnetic field as in our experiments. As shown in Fig. 2, however, a clear change was observed in the surface morphology of the film grown with a field of 14T. The edges of cube-shaped crystals softened and became rounded by

Fig. 2 Surface morphology of the Ti_2O_3 film electrodeposited (a) without a magnetic field and (b) with a field of 14T.

the magnetic field. This magnetic field effect was barely observed with a field of 1.5T. Moreover, no morphological change was observed with magnetic fields parallel to the faradaic current.

Electrodeposition includes mass-transfer, electron-transfer, and interface kinetic processes. When the deposition is carried out at a potential where the current is diffusion-controlled, a dendritic growth pattern is obtained⁷⁾. In this case, the MHD effect on the mass-transfer of Ti^+ is presumed to be dominant. In our experiments, the films were deposited at a potential giving kinetic-controlled current, therefore, the magnetic field is assumed to have af-

fecting the interface kinetic process, in which the growth units diffused along the growing interface and were crystallized at kinks or steps. The magnetic field was applied parallel to the working electrode, so that the MHD convection was induced along the Ti plate. It is concluded that this convection disturbed the interface diffusion process, and as a result, the crystal faces on the film surface became irregular.

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