—Communication—

Preparation of Cobalt Films by Electrodeposition at the Interface between Two Liquid Phases

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1. Introduction

The two-dimensional metallic deposit named as "metal leaf" grows by the cathodic reduction of a metal along the interface between an organic liquid insoluble in water and an aqueous solution of the metal^{1)~3)}. The authors found that film-like deposits, morphologically different from usual spoke-like metal leaves, could be obtained under limited conditions^{4),5)}, and recently, developed a new technique for continuously obtaining a very thin metallic film⁶⁾: a zinc film with a thickness of about 1 μm was grown uni-directionally along the n-butyl acetate/zinc sulfate solution interface. In the present study, the growth pattern and the morphology of cobalt films electrodeposited at the heptane/cobalt sulfate solution interface have been investigated.

2. Experimental

The apparatus used is shown in Fig. 1. The cell with a water-jacket was filled with an aqueous cobalt sulfate solution in the concentration range of 0.5 to 2 $\text{mol}\cdot\text{dm}^{-3}$, the surface of which was covered with a small amount of heptane. An aluminium foil 10 mm wide and 15 μm thick as a cathode was floated at the interface between the aqueous solution and the heptane. A cobalt plate as an anode was positioned vertically to the cathode so that applied current flowed only to the growing front of the film. Electrodeposition of cobalt films was conducted in the temperature range of 25 to 40 $^{\circ}\text{C}$, in the applied

Fig. 1 Experimental set-up.

voltage range of 4 to 8 V or the applied current range of 100 to 200 mA. The film growing at the interface was rolled onto the drum by a computer-controlled stepping motor so that the distance between the film and the anode was maintained at about 3 mm.

3. Results and Discussion

The growth morphology of a cobalt film depended on several factors. The film growing at 100 mA at 30 $^{\circ}\text{C}$ is shown in Fig. 2. In the initial stage of the electrodeposition, the film grew circularly to the anode, and then its width became narrow. When a part of the growing front of the film happened to be submerged in the aqueous solution, the part did not grow any longer. Therefore, the condition that the film can easily be floated at the interface by the interfacial tension is necessary for the film to continue to grow uniformly. The growth rate of the film was about 8 $\text{mm}\cdot\text{min}^{-1}$. The current efficiency, which was calculated from the weight of the film and the quantity of electricity passed, was 100 % unless very high voltage or current was applied. Assuming that the film is perfectly dense, the calculated thickness is 3 μm .

The organic liquid side of the film was

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Fig. 2 Growth morphology of a cobalt film. Applied current=100 mA, temperature=30 °C, CoSO_4 concentration=0.5 mol·dm⁻³

Fig. 3 Cross-sectional view of a cobalt film.

lustrous, but its aqueous solution side was sooty. This difference of the appearance was due to the surface structure of the film. The cross-sectional view of the film is shown in Fig. 3. The film was composed of two layers. The layer facing on the organic liquid is a thin compact film with a thickness of about 1 μm, and it is covered with very fine fur. The layer facing on the aqueous solution consists of less dense aggregates of spokes growing toward the aqueous solution, and accretions ride on the tips of the spokes. The thickness of the total layers was 65 μm. This value is

much higher than calculated one, 3 μm, suggesting that the layer facing to the aqueous solution side has a porosity of 97 %.

Two types of two-dimensional deposits, spoke-like and film-like, can be obtained by the electrodeposition at the interface between two liquid phases. It is known that the spoke-like growth is favored at high applied voltages or currents³³, consistent with the prediction from the diffusion-limited aggregation model⁷³. In the present study, too, spoke-like deposits preferentially grew at lower temperatures and at higher applied voltages or currents under the experimental conditions examined. Therefore, the electrodeposition of a film must be conducted at an applied voltage or current as low as possible and at a temperature as high as possible unless the volatilization of the organic liquid is so serious.

Cobalt films, as well as zinc films obtained in the previous study⁶³, could be electrodeposited uni-directionally at the heptan/aqueous CoSO_4 solution interface by choosing appropriate experimental conditions on temperature, CoSO_4 concentration and applied voltage or current. This technique has an advantage of obtaining metallic films a few micrometers in thickness without using any substrates for deposition. Therefore, the technique will be expected to be widely applied for the preparation of very thin metallic films.

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