Electrochemical Deposition of Metal Nitride Films in a Molten Chloride System

T. Goto, A. Niki, H. Tsujimura and Y. Ito

Department of Fundamental Energy Science,
Graduate School of Energy Science,
Kyoto University, Kyoto 606-8501, Japan

goto@energy.kyoto-u.ac.jp

1. Introduction

Nitride films are used as a surface protection material, a semiconductor material, an optical material and a magnetic material due to their physically and chemically excellent characteristic. To realize the excellent properties of nitrides, it is important to control the composition of nitrides precisely. For this purpose, electrochemical process would be applicable. From the background, we have newly proposed the electrochemical deposition of metal nitride films by using the reduction of ammonium ions in molten salts. In this report, as a model case, the electrochemical deposition of chromium nitrides on a nickel substrate was investigated in LiCl-KCl containing ammonium ions and chromium cations, in order to clarify the possibility of electrochemical deposition and control for chromium nitride deposition. Prior to the electrochemical deposition of chromium nitrides, electrochemical behaviors of ammonium ions and chromium cations were investigated by means of a cyclic voltammetry.

2. Experimental

Molten LiCl-KCl eutectic mixture was used as an electrolyte. All the experiments were performed under a dry Ar atmosphere. NH_4Cl and $CrCl_2$ were added directly into the melt as a nitrogen source and a chromium source, respectively. Ni plate was used as the working electrode. The counter electrode was a glassy carbon rod or a chromium plate. The reference electrode was an Ag^+/Ag electrode. All potentials are given with reference to a Li^+/Li electrode potential.

3. Results and discussion

It was indicated from the cyclic voltammogram for a Ni electrode that the reduction of both ammonium ions and chromium ions proceeded at potentials more negative than 1.7 V (vs. Li^+/Li). Based on the above result, potentiostaic electrolysis was conducted on Ni plate at 1.7 V for 30 min in a LiCl-KCl-$CrCl_2$(0.2 mol%)-NH_4Cl(0.1 mol%) melt. From the result of XRD analysis as shown in Fig. 1, it was confirmed that Ni surface was coated with Cr_2N. The concentration of nitrogen in the obtained nitride film increased as the applied potentials was more negative. Theses tendencies indicated that the concentration of nitrogen in the nitride film was controlled by the applied potentials. For investigating the morphology of the obtained film, the surface image and cross-section of the sample after potentiostatic electrolysis at 1.5 V was observed with SEM (Fig. 2). It is clearly seen that an adhesive coherent nitride film is formed on a nickel substrate and the thickness is about 10 □m. These results show that the new electrochemical deposition of metal nitride films is potentially applicable for rapid nitride film formation process.

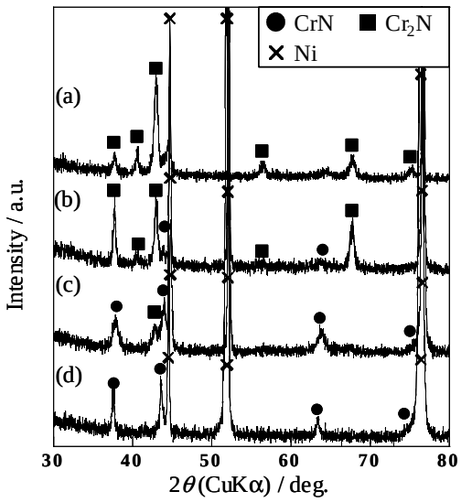

Fig. 1 XRD patterns of Ni samples after potentiostatic electrolysis at (a) 1.7 V (vs. Li^+/Li), (b) 1.6 V, (c) 1.5 V, and (d) 1.4 V in a LiCl-KCl-NH_4Cl(0.1 mol%)-$CrCl_2$(0.2 mol%) melt for 30 minutes at 723 K.

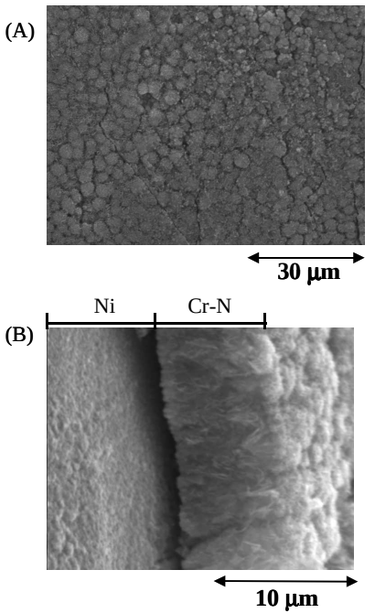

Fig. 2 Surface image (A) and cross sectional image (B) of Ni electrode after potentiostatic electrolysis at 1.5 V for 30 min at 723 K.

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