ELECTROCHEMICAL DEPOSITION OF METAL NITRIDE FILMS IN A MOLTEN CHLORIDE SYSTEM

Takuya Goto, Aiko Niki, Hiroyuki Tsujimura and Yasuhiko Ito

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

ABSTRACT

The electrochemical deposition of chromium nitride film on nickel electrode has been investigated in LiCl-KCl-NH4Cl-CrCl2 systems at 723 K. When a nickel electrode is cathodically polarized at potentials more negative than 1.7 V (vs. Li⁺/Li) in the melt, the reduction proceeds to form chromium nitride films on a nickel electrode. From the XPS and XRD results, it is confirmed that obtained films consists of CrN and C-N and that the composition of each film is effected by the applied potential values. The thickness of Cr-N formed at 1.5 V for 30 min is found to be about 10 μm from the result of a cross-sectional SEM image.

INTRODUCTION

Metal nitride coating is an attractive method for improving the properties of substrates surface. Since metal nitrides have various excellent properties such as high melting point, super hardness, wear resistance and highly chemical and physical stability under severe conditions. Thus, many processes for coating metal nitride are proposed and practically used. However, these methods such as ion plating, plasma process and spray method need high energy and complicated equipments. Harmful gas evolution is a drawback from the environmental point of view, since organic metals are used as precursors in the chemical vapor deposition process. In addition, it is difficult for the processes to form nitride films onto substrates with large area or with complex surface morphology. From the background, we have newly proposed the new electrochemical nitride coating process for improving the disadvantages of conventional processes. The followings are the concepts of the proposed process. A molten LiCl-KCl is used as a model electrolyte. Ammonium chloride (NH4Cl) and metal chloride (MClx) are used as nitrogen source and metal source, respectively, and dissolved in the melt to produce NH4⁺ and Mx⁺. When a working electrode (substrate material) is cathodically polarized in the melt, the reduction of NH4⁺ and Mx⁺ proceeds to produce metal nitride film (MxN) on the substrate. In this paper, in order to clarify the possibility of the electrochemical metal nitride deposition in molten salt system, the electrochemical deposition of chromium nitride on a nickel substrate was selected as a model case and the following experiments were carried out. Firstly, electrochemical behaviors corresponding to the electrochemical coating of chromium nitride have been examined by cyclic voltammetry. A nickel was used as a cathode and potentiostatic electrolysis of the cathode was carried out at various potentials in order to clarify the relationships between applied potentials and nitrogen concentration of nitride layer.
EXPERIMENTAL

All experiments were conducted in an argon atmosphere using a glove box with a continuous gas refining instrument. Details of the experimental procedure are presented in our previous paper [1]. An electrochemically polished nickel plate (The Nilaco Co., Ltd. 99.8 %) was used as a working electrode. Reagent grade LiCl and KCl was dried under vacuum for more than 72 h at 473 K in order to remove water. The eutectic mixture (59 mol % LiCl, 41 mol % KCl) was then melted in a high purity alumina crucible. Ammonium chloride (NH₄Cl) was used as an ammonium ion source. Chromium dichloride (CrCl₂) was used as a chromium cation source. Electrochemical measurements and electrochemical coating were conducted using a potenti/o-galvanostat (Hokuto Denko Co., Ltd.: HA-301) combined with a function generator (Hokuto Denko Co., Ltd.: HB-104). Morphologies of samples were observed through a scanning electron microscope (SEM) (Hitachi Co., Ltd.: S-2300). The obtained films were also characterized by X-ray diffraction (XRD) (Rigaku Co., Ltd.: Multiflex) using Cu Kα line as the X-ray source.

RESULTS AND DISCUSSION

Electrochemical behavior of ammonium ions and chromium ions. Cyclic voltammetry was carried out in order to investigate the electrochemical behavior of chromium ions and ammonium ions. Figure 1 shows cyclic voltammograms for a nickel electrode in LiCl-KCl-CrCl₂ before and after adding NH₄Cl into the melt. The scanning direction goes from the rest potential to the cathodic potential direction and reverses back the sweep direction. Before adding NH₄Cl, the cathodic currents (peak A) are observed at 1.7 V. From the reported value of the reduction of Cr(II) in LiCl-KCl, the formal standard potential of Cr(II)/Cr(0) is estimated to be 1.7 V in the melt containing CrCl₂ 0.2 mol% [2]. The currents observed at 1.7 V correspond to the deposition of chromium melt, which is expressed as the following equation (1):

\[
\text{Cr(II)} + 2 \text{e}^- \rightarrow \text{Cr}
\]  

(1)

After adding NH₄Cl, new two cathodic waves (peak B and C) are observed at 2.4 V and 1.7 V, respectively. Cathodic wave is not observed at 2.4 V before adding NH₄Cl. This indicates that the reduction of ammonium ions proceeds at potentials more negative than 2.4 V, which is expressed as the following equation (2):

\[
\text{NH}_4^+ + \text{e}^- \rightarrow \text{NH}_3 + \frac{1}{2} \text{H}_2
\]  

(2)

Considering the peaks A and C, the reduction of chromium cations proceeds to form chromium metal at potentials more negative than 1.7 V. Therefore, one can expect that the reduction of ammonium ions and chromium cations proceeds to form chromium nitride according to the following reaction scheme.

\[
x \text{Cr(II)} + \text{NH}_4^+ + (2x + 1) \text{e}^- \rightarrow \text{Cr}_x\text{N} + 2 \text{H}_2
\]  

(3)
Electrochemical reduction of ammonium ions. Prior to the electrochemical deposition of chromium nitride on a nickel substrate, the electrochemical surface nitriding of a chromium metal was examined in LiCl-KCl-NH₄Cl in order to clarify that the nitride formation proceeds by the reduction of NH₄⁺. In order to confirm this, the following potentials were selected; 0.5 V, 1.0 V and 1.5 V where potentials were considered to be enough negative to form chromium nitrides. Figure 2 shows XRD patterns of chromium specimens after potentiostatic electrolysis for 1 hour at (a) 1.5 V, (b) 1.0 V, (c) 0.5 V and (d) the sample immersed in LiCl-KCl-NH₄Cl (1.0 mol %) melt at 723 K. The main diffraction peaks in Fig. 2 (a) were identified as Cr₂N [3] and the minor peaks were originated from a Cr substrate [4]. In Fig. 2 (b), peaks corresponding to CrN [3] are newly observed in addition to peaks coming from Cr₂N. The peak intensity corresponding to a Cr substrate becomes smaller compared with those of Fig. 2 (a). This result suggests that the thickness of the nitride layer increases as the applied potential become more negative. As shown in Fig. 2 (c), peaks corresponding to the chromium substrate disappear and the CrN peak becomes more distinctly compared with other two samples. This result suggests that the thickness of the nitride layer and the concentration of nitrogen in the film increase as the applied potential are more negative. On the other hand, XRD patterns in Fig. 2 (d) identified as Cr₂O₃ [3]. The nitride formation is not considered to proceed that Cr electrode directly reacted with NH₃ by the decomposition of NH₄Cl. In general, temperature of thermal nitridation of chromium in NH₃ needs above 753 K [5]. Thus, the obtained nitride films in Fig. 2 are electrochemically formed in LiCl-KCl-NH₄Cl system.

![Cyclic voltammograms for Ni electrode in LiCl-KCl-NH₄Cl melt before and after containing CrCl₂ and at 723 K. Scan rate is 0.1 V s⁻¹.](image)
Electrochemical deposition of chromium nitride film on a nickel electrode. The results of previous section showed that the electrochemical reduction of $\text{NH}_4^+$ in a molten chloride is necessary to form chromium nitride. On the other hand, in LiCl-KCl-NH$_4$Cl-CrCl$_2$, it is indicated from the cyclic voltammograms for a Ni electrode (Fig. 1) that the formation of chromium metal proceeds at potentials more negative than 1.7 V. Thus, the reduction of both ammonium ions and chromium ions proceeded at potentials more negative than 1.7 V to form chromium nitride on a nickel electrode. In order to confirm this, potentiostatic electrolysis was conducted on Ni plate at 1.7 V, 1.6 V, 1.5 V and 1.4 V for 30 min in a LiCl-KCl-CrCl$_2$ (0.2 mol%)-$\text{NH}_4$Cl (0.1 mol%) melt. The main diffraction peaks in Fig. 3 (a) were identified as Cr$_2$N [3] and the minor peaks were originated from a Ni substrate [4]. In Fig. 3 (b), peaks corresponding to CrN [3] are newly observed in addition to peaks coming from Cr$_2$N. The peak intensity corresponding to Cr$_2$N becomes stronger compared with those of Fig. 3 (a). This result suggests that the thickness of the nitride layer increases as the applied potential become more negative. As shown in Fig. 3 (c), main peaks correspond to CrN and minor peaks corresponds Cr$_2$N. In Fig. 3 (d), the peaks corresponding to Cr$_2$N almost disappear and the CrN peak becomes more
distinctly compared with other three samples. This result suggests that the thickness of the nitride layer and the concentration of nitrogen in the film increase as the applied potential are more negative. From the result of XRD analysis as shown in Fig. 3, it is confirmed that Ni surface is coated with chromium nitride. The concentration of nitrogen in the obtained nitride film increased as the applied potentials was more negative. Theses tendencies indicate that the concentration of nitrogen in the nitride film is controlled by the applied potentials.

Figure 3. 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-NH₄Cl (0.1 mol%)–CrCl₂ (0.2 mol%) melt for 30 min at 723 K.

For investigating the morphology of the obtained film, the cross-section of the sample after potentiostatic electrolysis at 1.5 V was observed with SEM (Fig. 4). It is clearly seen that an adhesive coherent nitride film is formed on a nickel substrate and the thickness is about 10 μm. These results show that the new electrochemical deposition of metal nitride films is potentially applicable for rapid nitride film formation process.
CONCLUSIONS

Electrochemical deposition of metal nitride films in a molten chloride system has been proposed and experimentally confirmed the possibility of the electrochemical deposition of nitride film by showing the electrochemical deposition of chromium nitride on a nickel substrate as a model. The followings are summarized as follows:

1) Electrochemical surface nitriding proceed at potentials more negative than 1.5 V with the use of reduction of ammonium ions to form chromium nitride on chromium surface in LiCl-KCl-NH₄Cl. The process did not proceed by immersing a chromium electrode in the melt containing ammonium ions.

2) When a nickel electrode was cathodically polarized at potentials more negative than 1.7 V (vs. Li⁺/Li) in LiCl-KCl-NH₄Cl-CrCl₂, the reduction proceeds to form chromium nitride films on a nickel electrode.

3) The concentration of nitrogen in the obtained nitride film increased as the applied potentials was more negative.

4) The thickness of chromium nitride formed at 1.5 V for 30 min was estimated to be 10 μm.

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