

# A New Electrodeposition Process of Metallic Ti Films Utilizing Water-soluble KF–KCl Molten Salts

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## Abstract

Electrodeposition of metallic Ti using water-soluble KF–KCl molten salt electrolyte was investigated. Ti films were electrodeposited on Ni substrate in a eutectic KF–KCl (45:55 mol%) melt containing  $K_2TiF_6$  and Ti sponge at 923 K. Cyclic voltammetry suggested the deposition of Ti metal at the potential more negative than 0.4 V (vs.  $K^+/K$ ) and the redox reaction of Ti(IV)/Ti(III) around 1.8 V. The analytical results of SEM, EDX and XRD revealed that dense and smooth film of Ti metal with 30  $\mu\text{m}$  thickness was electrodeposited by galvanostatic electrolysis at current density of 100  $\text{mA cm}^{-2}$  for 25 min.

## Introduction

Titanium metal has superior properties such as high strength-to-weight ratio, corrosion resistance, heat resistance, and biocompatibility. However, the current production method has several drawbacks due to high production cost of the Kroll process and poor workability of titanium, which has prevented the widespread use of titanium. Thus, the development of a new manufacturing process of titanium is demanded.

Plating metallic titanium on general substrates is a promising approach to utilize the superior properties of titanium. Currently, several PVD methods are commonly used for a coating of some titanium compounds. However, the deposition onto a substrate with complicated shape is difficult for the PVD methods. Electroplating in molten salts has been expected as a coating method of titanium for various shapes. The electrodeposition of titanium metal has been studied in high-temperature molten salts. In previous studies, chloride melts<sup>1–5</sup>, fluoride melts<sup>6–11</sup>, and mixed fluoride–chloride melts<sup>12–16</sup> were investigated as electrolytes. Generally, compact and smooth Ti films were obtained from fluoride melts such as LiF–NaF–KF<sup>6–9</sup> or fluoride–chloride melts such as NaCl–KCl–NaF<sup>14</sup>. The main problem using fluoride based melts is the difficulty to remove the solidified salt from the obtained Ti films by water washing, because most fluoride salts have very low solubility in water

(LiF; 0.13, NaF; 4.15, MgF<sub>2</sub>; 0.13, CaF<sub>2</sub>; 0.0016 g per 100 g H<sub>2</sub>O)<sup>17</sup>). Concerning the fluoride-chloride melts, the influence of F<sup>-</sup> ion concentration on the morphology of the Ti deposits has been investigated by several researchers. Song *et al.* reported that the addition of KF into KCl–NaCl up to a molar ratio of [F<sup>-</sup>]/[Ti<sup>n+</sup>] = 6 led to the deposition of Ti metal with fine crystal grains, and that it is advantageous for the formation of compact and smooth Ti films<sup>15</sup>).

From this background, we have proposed a new process for the electrodeposition of Ti using KF–KCl as a molten salt electrolyte<sup>18</sup>). Among the alkali and alkaline earth fluorides, KF has an exceptionally high solubility in water (101.6 g per 100 g H<sub>2</sub>O)<sup>17</sup>). However the use of KF single melt is problematic, owing to the high melting point of KF (1131 K). The use of binary KF–KCl melts (melting point = 878 K at the eutectic composition)<sup>19</sup>) enables to lower the melting point without losing good water-solubility since KCl also has a high solubility in water (35.9 g per 100 g H<sub>2</sub>O)<sup>17</sup>). On the basis of previous studies<sup>6–16</sup>), Ti(III) ions were obtained by the comproportionation reaction (1).



In the present study, electrochemical behavior of Ti ions and electrodeposition of Ti metal were investigated in a KF–KCl melt after the addition of K<sub>2</sub>TiF<sub>6</sub> and sponge Ti. The deposited samples obtained by galvanostatic electrolysis were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).

## Experimental

A schematic representation of the experimental apparatus is shown in Fig. 1. Reagent grade KF (Wako Pure Chemical Co., Ltd., > 99.0%) and KCl (Wako Pure Chemical Co., Ltd., > 99.5%) were mixed to the eutectic composition (molar ratio of KF:KCl = 45:55, melting point = 878 K<sup>19</sup>), 400 g) and loaded in a nickel crucible (Chiyoda Industry Co., Ltd., outer diameter: 96 mm, and height: 102 mm). The mixture in the crucible was first dried under vacuum at 453 K for 72 h. The crucible was placed at the bottom of a stainless steel vessel in an air-tight Kanthal container and further dried under vacuum at 773 K for 24 h. The electrochemical measurements were conducted in a dry Ar atmosphere at 923 K in a glove box. 0.10–2.0 mol% K<sub>2</sub>TiF<sub>6</sub> (Morita Chemical Industry Co., Ltd., > 97.5%) and 0.033–1.3 mol% Ti sponge (Wako Pure Chemical Co., Ltd., > 99%) were added to the melt.

Electrochemical measurements and galvanostatic electrolysis were conducted by a three-electrode method using a electrochemical measurement system (Hokuto Denko Corp., HZ-7000). The working electrodes were a Ni plate (Nilaco Corp., 5 mm × 10 mm, thickness: 0.1 mm, > 99%), a Mo flag (Nilaco Corp., diameter: 2.0 mm, thickness: 0.1 mm, 99.95%), and a Pt flag (Nilaco Corp., diameter: 2.0 mm, thickness: 0.1 mm, 99.98%). The structure of the flag electrodes was reported in our previous paper<sup>20</sup>). In order to remove the surface oxide film, a Ni plate for electrodeposition was electropolished in 50 wt% sulfuric acid at 200 mA cm<sup>-2</sup> for 10 s, dipped in aqueous solution containing sodium bifluoride, and followed by washing in hydrochloric acid of pH = 4.0, at room temperature. The Ni plate was then washed by ethanol. A Ti rod (Nilaco Corp., diameter: 3.0 mm,

99.5%) was used as a reference electrode. The potential of the reference electrode was calibrated with reference to a dynamic  $K^+/K$  potential estimated by cyclic voltammetry on a Mo flag electrode. The counter electrode was Ti plate (Nilaco Corp., 10 mm × 10 mm, thickness: 1.0 mm, 99.5%). The temperature of the melt was measured by a type K thermocouple. The electrolyzed samples on the Ni plates were soaked in distilled water at 333 K for 1 h to remove the salt adhered on the deposits. The cross-sections of the samples were studied by SEM (Keyence Corp., VE-8800). For the observation, the samples were embedded in acrylic resin and polished with emery papers and buffing compounds. After polishing, the samples were coated with Au by an ion sputtering apparatus (Hitachi, Ltd., E-1010) to give conductivity. The deposits were also characterized by EDX (AMETEK Co., Ltd., EDAX Genesis APEX2) and XRD (Rigaku Corp., Ultima IV, Cu-K $\alpha$  line).

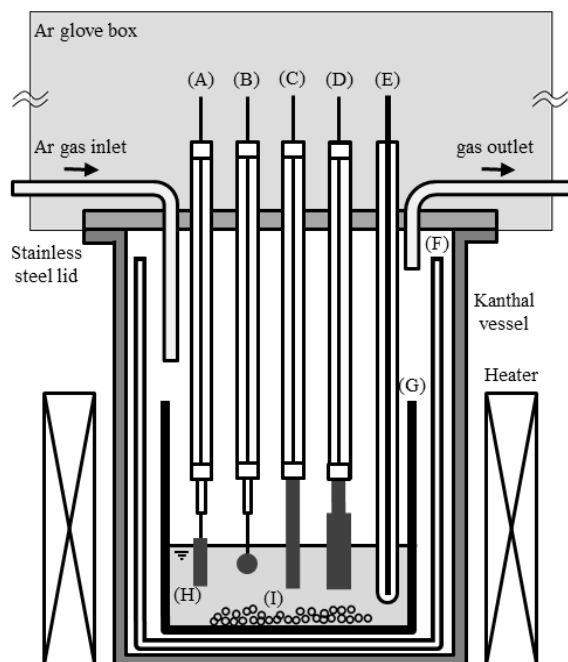


Fig. 1 A schematic drawing of the experimental apparatus for electrochemical measurements. (A) Ni plate electrode, (B) Mo and Pt flag electrodes, (C) Ti rod electrodes, (D) Ti plate electrode, (E) thermocouple, (F) stainless steel inner vessel, (G) Ni crucible, (H) molten KF–KCl, and (I) Ti sponge.

## Results and Discussion

### Electrochemical behavior of Ti(III) ions

Fig. 2 shows the cyclic voltammograms for a Pt flag electrode scanned from the open-circuit potential to the positive direction after the addition of 0.50 mol%  $K_2TiF_6$  and 0.17 mol% Ti sponge at 923 K. A pair of redox currents are observed around 1.8 V, which is explained by the redox reaction of Ti(IV)/Ti(III).



The redox reaction is reversible process because the peak potentials of these currents were constant at various scan rates. In the present experiment, the open-circuit potential was observed at approximately 0.7 V. Since this value is much more negative than the redox potential of Ti(IV)/Ti(III), most of the Ti ions exist as Ti(III) in the melt.

Fig. 3 shows the cyclic voltammograms for a Mo flag electrode scanned from the open-circuit potential to the negative direction before (dashed curve) and after (solid curve) the addition of 0.10 mol%  $K_2TiF_6$  and 0.033 mol% Ti sponge. Only in the voltammogram after the addition, cathodic

current flowing from approximately 0.4 V (current (a)) is observed. After the reversal of scanning direction, the corresponding anodic current is also observed (current (a')). This result suggests that Ti metal is deposited from Ti(III) ions at potentials more negative than 0.4 V.



Additional anodic current is also observed from 0.5 V (current (b)). From the phase diagram of the Ti–Mo system, titanium forms a solid solution alloy with Mo at 923 K<sup>21</sup>). Thus, the observed current (b) is likely to be associated with the dissolution of Ti from the Ti–Mo alloy.

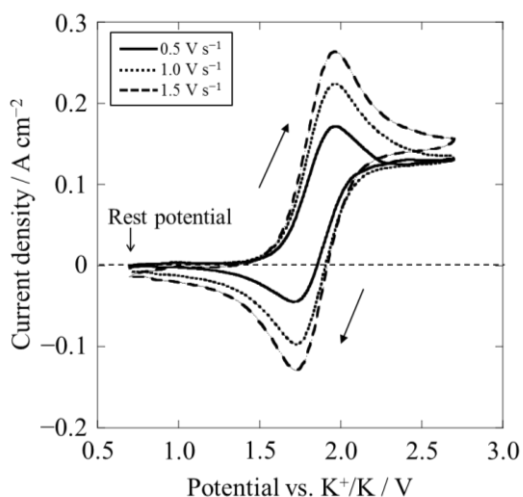
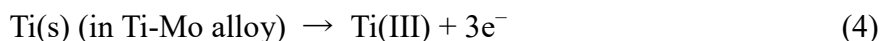


Fig. 2 Cyclic voltammograms for a Pt flag electrode in molten KF–KCl after the addition of  $\text{K}_2\text{TiF}_6$  (0.50 mol%) and Ti sponge (0.17 mol%) at various scan rates at 923 K.

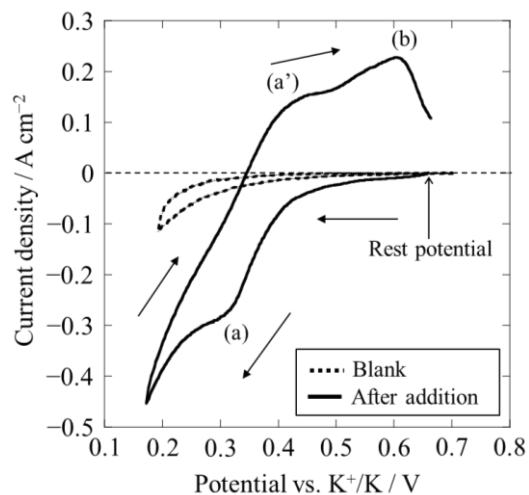


Fig. 3 Cyclic voltammograms for a Mo flag electrode in molten KF–KCl before and after the addition of  $\text{K}_2\text{TiF}_6$  (0.10 mol%) and Ti sponge (0.033 mol%) at 923 K. Scan rate:  $0.20 \text{ V s}^{-1}$ .

### Electrodeposition of titanium metal

The sample was prepared by galvanostatic electrolysis on a Ni plate electrode at 923 K. The electrolysis was carried out at current density of  $100 \text{ mA cm}^{-2}$  for 25 min. As seen from the surface SEM image in Fig. 4(a), the film is densely packed with compact crystal grains. From the cross-sectional SEM image at the center of the sample plates in Fig. 4(b), the film has smooth surfaces and thickness around  $30 \text{ }\mu\text{m}$ . EDX analysis revealed that the film was consisted of only Ti, and that all the components of the molten salt electrolyte (K, F, and Cl) were below the detection limits. Thus, the adhered salt on the Ti deposit was successfully removed only by water washing.

Since deposition of crystalline titanium metal is confirmed in the XRD patterns (Fig. 3(c)), the reduction current observed at more negative than 0.4 V is confirmed to be due to the deposition of Ti metal. The current efficiency for Ti deposition calculated from the weight increase was 94%. Under the assumption of a three-electron reaction, the theoretical thickness of the Ti layer is calculated to be 55  $\mu\text{m}$ , which is larger than the observed thickness about 30  $\mu\text{m}$ . This could be attributed to the uneven distribution of current, i.e., high current densities at the edges and low current densities at the center.

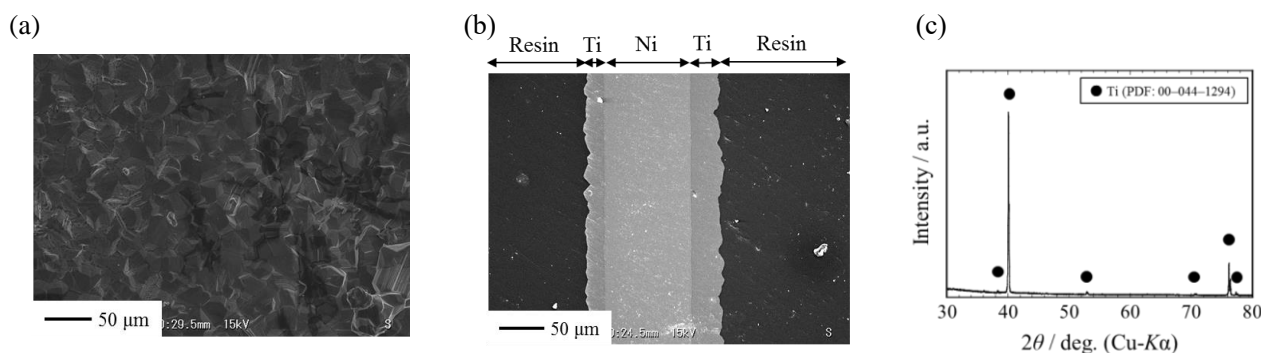


Fig. 4 (a) A surface SEM image, (b) a cross-sectional SEM image, and (c) XRD pattern of the sample obtained by galvanostatic electrolysis of a Ni plate electrode at  $-100 \text{ mA cm}^{-2}$  for 25 min in molten KF–KCl after the addition of  $\text{K}_2\text{TiF}_6$  (2.0 mol%) and sponge Ti (1.3 mol%) at 923 K.

## Conclusions

Electrodeposition of titanium metal was investigated in a KF–KCl molten salt containing Ti(III) ions at 923 K. The Ti(III) ions were prepared by the addition of 0.10–2.0 mol%  $\text{K}_2\text{TiF}_6$  and 0.033–1.3 mol% Ti sponge. The electrochemical behaviors were investigated by cyclic voltammetry. The redox current peaks of Ti(IV)/Ti(III) were observed around 1.8 V (vs.  $\text{K}^+/\text{K}$ ) at a Pt flag electrode. Cathodic current corresponding to the deposition of metallic Ti was observed at potentials more negative than 0.4 V at a Mo flag electrode. The solidified salt was successfully removed from the electrode only by washing with water. The deposit obtained by galvanostatic electrolysis was analyzed by surface and cross-sectional SEM, EDX, and XRD. The film deposited at current density of  $100 \text{ mA cm}^{-2}$  had smooth surfaces and approximately 30  $\mu\text{m}$  thickness. XRD analysis revealed that crystalline metallic titanium was deposited.

## Acknowledgement

A part of this study was conducted as collaborative research with Sumitomo Electric Industries, Ltd.

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