

**Electrodeposition of Titanium Metal
from Fluoride–Chloride Mixed Molten Salts
Consisting of Single Cations**

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Chapter 1

General Introduction

1.1 Features and Applications of Titanium Metal

Titanium is a promising material due to its unique properties such as high heat resistance, corrosion resistance, strength to weight ratio and biocompatibility [1]. The high heat resistance is related to its high melting point of 1940 K. Titanium is highly reactive with oxygen and is easily oxidized to form passive oxide films on the surface, leading to the high corrosion resistance. Since the density of titanium is as low as 4.54 g cm^{-3} at 293 K, the specific strength of titanium is about 3 times higher than that of aluminum and 2 times higher than that of iron [2]. Owing to these properties, titanium has been used in various fields such as airplane, industrial plant, and consumer products. Titanium is generally regarded as a rare metal, however, its raw materials such as TiO_2 and FeTiO_3 are relatively abundant in the earth's crust. In fact, the crustal abundance of titanium is estimated to be 0.44% [3]. This value is more than 40 times larger than those of commonly used copper and nickel.

Fig. 1-1 shows shipment share of titanium wrought materials by applications in Japan in 2018 [4]. The largest field is the chemical plant due to the desirable properties of titanium-based materials. The corrosion resistance of titanium against seawater is much higher compared with other metals such as stainless steel. Thus, titanium-based compounds are often used as seawater-resistant materials for desalination equipment, seawater condenser pipes, ships, bridges, etc. Titanium and its alloys are also widely used in airplanes and automobiles as frames and engine parts because of their high specific strength and heat resistance. In these applications, the weight

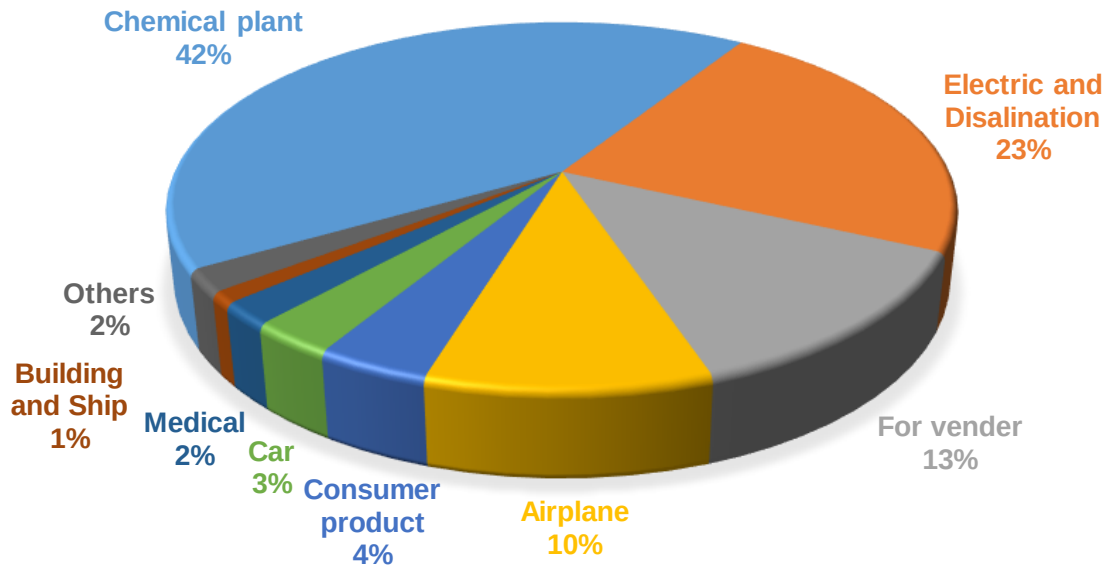


Fig. 1-1 Shipment share of titanium wrought materials by applications in Japan in 2018 [4].

reduction can improve the fuel efficiency. Incidentally, a large amount of sponge titanium exported from Japan is used for airplane materials whose demand is globally increasing. Furthermore, titanium is also used in consumer products including watches and glasses, in which its properties of high biocompatibility and durability are utilized. In particular, titanium is often used in the medical field as implants such as artificial teeth and bones. Although titanium has various attractive properties, there are two problems preventing the widespread use of titanium. One is low productivity of the current titanium smelting method. The other is high processing cost due to the poor workability of titanium. For example, the price of titanium plates in the US market is about 25 \$ kg⁻¹ (March 2019) [4] which is much higher than that of cold-rolling stainless steel used as building materials (*ca.* 3 \$ kg⁻¹ as of September 2019 in the Tokyo market) [5]. Therefore, to further spread titanium-based materials in various fields, it is necessary to develop novel titanium smelting and processing methods with higher productivity and lower production cost.

1.2 Smelting and Processing of Titanium Metal

The Kroll process is widely and only used as the industrial titanium smelting method, in which titanium is produced by reduction of titanium tetrachloride using magnesium metal [1,6–8].

Fig. 1-2 shows a flowchart of the Kroll process [1].

In general, ilmenite (chemical formula: FeTiO_3) is mined as a dominant titanium resource all over the world. Since the ilmenite is a complex oxide of titanium dioxide and iron oxide, the iron component has to be removed beforehand. After the removal of iron oxide, the produced rutile (TiO_2) called a synthetic rutile. At present, three types of raw materials, synthetic rutile, natural rutile, and titanium slag (low grade of titanium oxide), are used in the Kroll process. The Kroll process is mainly divided into four steps: chlorination, reduction, molten salt electrolysis, and processing. The detailed features for each step are summarized as follows.

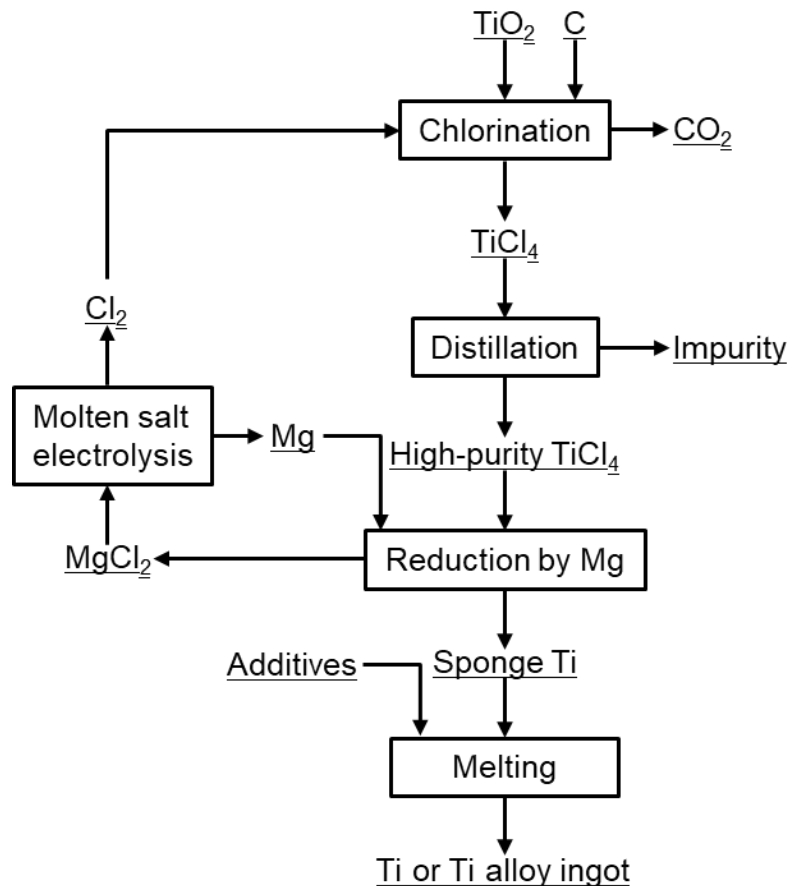


Fig. 1-2 A process flowchart of titanium production by the Kroll process [1].

(1) Chlorination step

Firstly, in the chlorination process, the titanium concentrates are reacted with cokes and chlorine gas at approximately 1273 K to synthesize titanium tetrachloride:



Since the obtained titanium tetrachloride contains a large amount of impurities derived from the concentrates, purification is conducted by continuous distillation to achieve over 99.99% purity.

(2) Reduction step

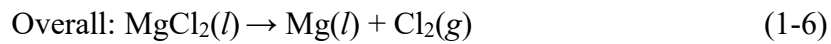
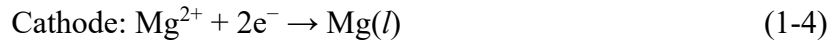
Secondly, in the reduction step, the titanium tetrachloride is reduced by magnesium metal at around 1173 K to produce metallic titanium.



This reaction is performed by dropping liquid titanium tetrachloride to molten magnesium in a steel reactor. Before the dropping of titanium tetrachloride, molten magnesium is put in the container filled with argon gas. Since the temperature of the inner wall of the container rises due to the exothermic reduction reaction of titanium tetrachloride, the dropping rate must be limited in order to prevent the perforation of container. In other words, the reaction rate is determined by the heat removal from the container. The obtained sponge-like titanium contains magnesium metal and magnesium chloride in its void space. These magnesium-based compounds are evaporated and separated in vacuum. Higher temperature and longer time operation are also inevitable for the vacuum separation. Moreover, the reduction step is a batch type process. It takes about 10 days to complete the reaction producing approximately 10 tons of sponge titanium.

(3) Molten salt electrolysis

Most of the recovered magnesium chloride is used to produce magnesium metal and chlorine gas by molten salt electrolysis.



The metallic magnesium is reused for reduction of titanium tetrachloride, and the chlorine gas for chlorination of titanium concentrates. The molten salt electrolysis is carried out at around 925 K in $\text{MgCl}_2\text{--NaCl--KCl}$ bath containing some fluorides. The electrolysis is generally conducted with the multi-polar electrode system to increase the productivity. The produced magnesium droplet is collected to a cathode room and transferred to the reduction reactor. The recycle use of magnesium chloride secures the high purity of the magnesium reductant and the produced sponge titanium.

(4) Processing step

Finally, the produced sponge titanium is cut by a crusher to a certain size. An ingot of titanium or titanium-alloy is obtained by melting the compacts prepared by pressing sponge titanium with/without alloying elements in a vacuum arc furnace. A titanium ingot is also produced by directly melting sponge titanium in an electron beam furnace. The titanium ingot is homogenized by secondary melting, and then further processed by rolling, forging, etc. to produce final products.

Fig. 1-3 shows relative cost factors for 1 inch-thickness of titanium-based alloy plate, which is used for various applications such as airplane. The fabrication process of 1-inch plate requires the highest cost, followed by the magnesium reduction process and the melting process. Here, most

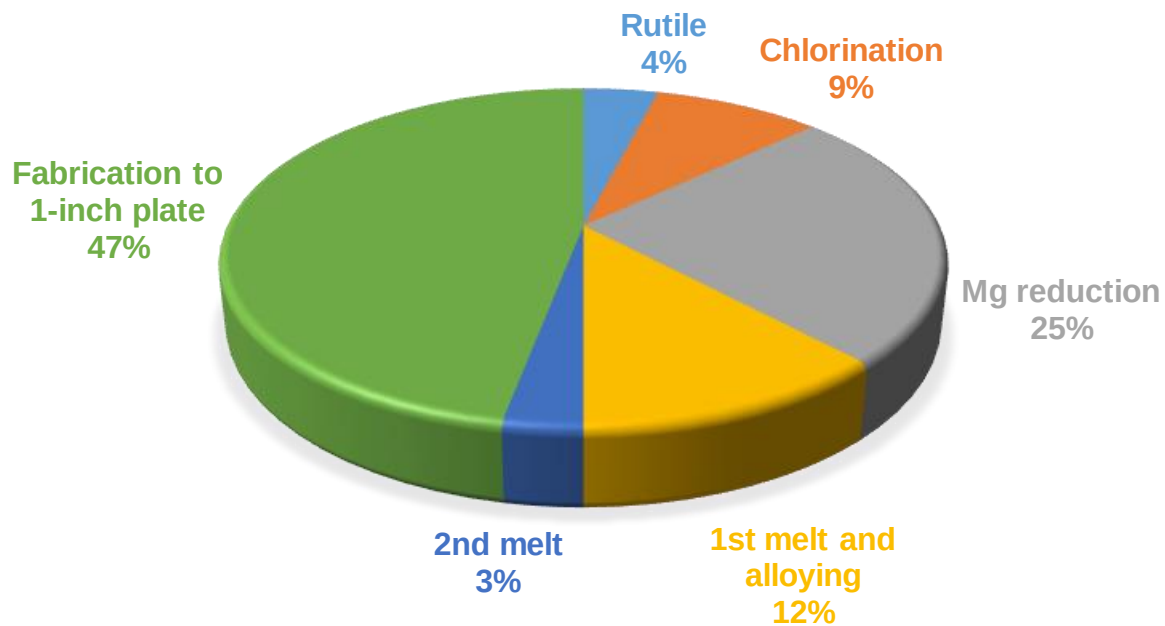


Fig. 1-3 Relative cost factors for 1 inch-thickness Ti-based alloy plate [6].

of the magnesium reduction cost is occupied by the production of metallic magnesium via molten salt electrolysis, and more than half of the total electric power for the whole process is consumed in the electrolysis process. The titanium processing requires special technique because of the high deformation resistance and the high strength of titanium. In addition, since titanium is highly reactive with oxygen, a continuous removal of the oxide film on the surface is needed during the processing. These processing difficulties result in the high cost of 1-inch plate fabrication.

To summarize, the Kroll process has both many advantages and disadvantages. The advantages are the production of high-purity titanium, easy separation of the produced titanium from reactants, and the established recycling process of by-products. Examples of the problems are low productivity due to the batch-type process, and large electricity consumption during the electrolysis. Moreover, since production of the Kroll process is sponge titanium, the melting and fabrication processes are necessary, which naturally leads to the high total production cost and the high price of final products.

1.3 Various Plating Methods

Generally, plating methods are classified into two types: “dry plating” and “wet plating”. Principles and features are described below [9,10].

1.3.1 Dry Plating

Dry plating describes a variety of plating methods which do not use any solvents. It is further categorized into a physical vapor deposition (PVD) and a chemical vapor deposition (CVD). PVD is a method of depositing a target metal on a substrate by physical methods such as heating and sputtering. CVD is a method to deposit a metal by reacting or pyrolyzing a gaseous compound on a heated substrate.

PVD includes vacuum vapor deposition, ion plating, and sputtering. Fig. 1-4 shows schematic illustrations of the principles of various PVD methods. In a vacuum deposition, a target metal is heated and evaporated in a high vacuum container. The evaporated metal is deposited on a cooled substrate. In an ion plating, thermally-evaporated target metal is ionized by plasma, a cathodic substrate is bombarded with the produced metal ions to deposit as the metal. In a sputtering method, the metal surface is hit by ionized gas atoms, and the sputtered metal atoms are deposited on a substrate. By using these dry plating methods, a high-purity and uniform film can be obtained. However, since the plating rate is very slow, it is difficult to prepare thick films. Therefore, these dry plating methods are used to deposit thin films with several micron meter thickness. Moreover, the difficulty in upsizing and the high energy consumption increase the plating cost. In addition, in some cases, thermal damage to the substrate becomes a problem.

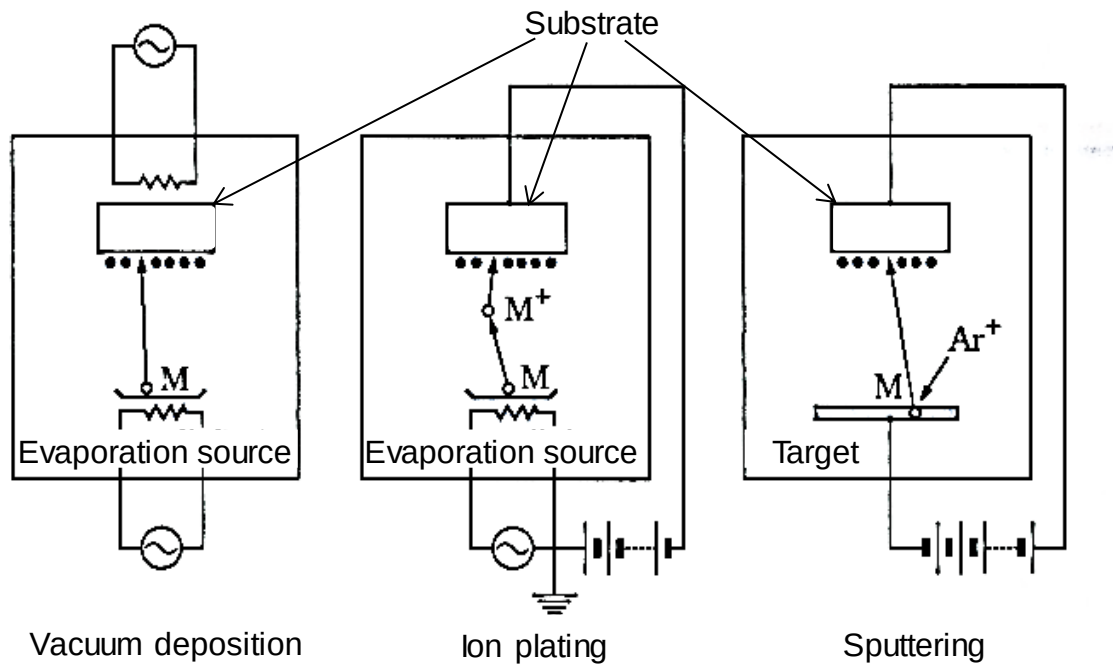


Fig. 1-4 Schematic illustrations for the principles of PVD processes.

1.3.2 Wet Plating

In general, wet plating is conducted in electrolytes, typically aqueous electrolytes. Organic solvents, room-temperature molten salts, and high-temperature molten salts are also used as electrolytes for wet plating, though they are not common. Wet plating is divided into two major types: “electroplating” and “electroless plating”. Fig. 1-5 shows schematic illustrations for the principles of (a) electroplating and (b) electroless plating.

In an electroplating, a cathode substrate is immersed in an electrolyte containing metal ions. Direct current is supplied from an external power source and the metal ions are reduced to metal on the surface of the cathode substrate.



The same metal or a carbon-based electrode is often used as an anode, and the metal dissolution or gas evolution occurs at the anode, respectively. In an electroplating, an external power source is

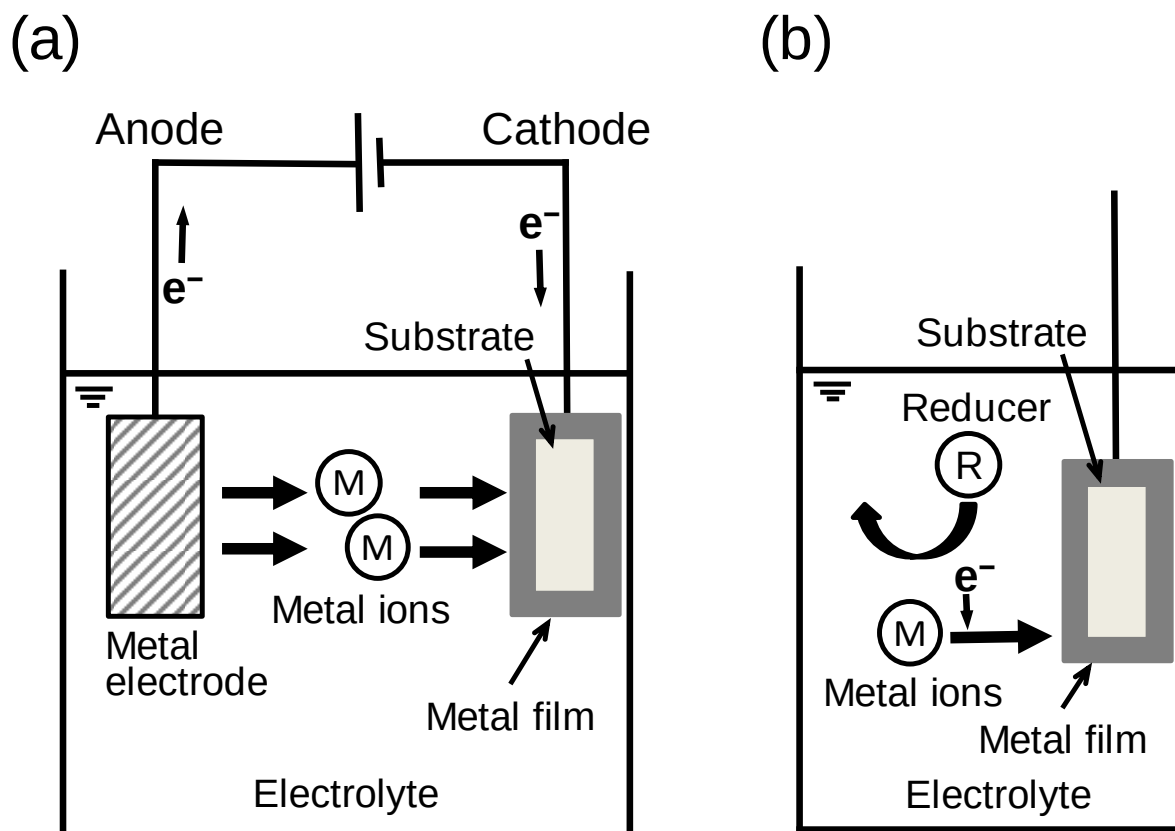


Fig. 1-5 Schematic illustrations for the principles of (a) electroplating and (b) electroless plating processes.

needed, and only conductive materials can be used as the substrate. In some cases, the uniformity of the formed film is poor due to uneven current distribution.

Electroless plating is a method of plating metal by chemical rather than electrical means, in which metal ions and a reducing agent are added to an electrolyte. The metal ions are reduced by the reducing agent. A uniform film can be easily obtained, and a non-conductive material can be used as the substrate. When the substrate itself is used as the reducing agent, it is called displacement plating. In the electroless plating, it is necessary to prepare a suitable reducing agent for the objective metal ions. The existing problems of the difficulty in obtaining thick films and the high plating cost are attributed to the necessity of sequential addition of the reducing agent.

1.3.3 Applicability of Plating Methods to Titanium Metal

The unique surface properties of metallic titanium such as high corrosion resistance, heat resistance, and biocompatibility are utilized in many application fields. One possible solution to address the high cost and low workability of titanium is the establishment of a novel titanium plating method which can be used for inexpensive substrate having good workability. For most applications, the surface film as thin as several tens micrometers is enough to provide the surface properties of titanium. Such a plating method will realize more widespread use of titanium metal.

Although the dry plating of titanium metal has been partly put into the practical use for semiconductor applications, the maximum film thickness is about 5 μm [11]. For many applications, this is not enough to utilize the surface properties of titanium. Also, the dry plating of titanium is unlikely to be widely used from the viewpoint of cost. In addition, the dry plating cannot be applied for a substrate with a complex shape. In wet plating methods, electroless plating is difficult for metallic titanium due to the negative redox potential. On the other hand, electroplating of titanium has been reported to be possible in proper electrolyte.

Considering these points, electroplating is the best choice for titanium plating. In the literature, organic solvents [12,13], room temperature molten salts [14], and high temperature molten salts [15–46] have been studied as electrolytes for titanium electrodeposition. However, when organic solvents or room temperature molten salts were used, only titanium-based alloys or uncertain compounds containing titanium element were obtained. So far, metallic titanium has been only obtained from high-temperature molten salts.

1.4 Electrodeposition of Titanium Metal from High-Temperature Molten Salts

In previous studies on electrodeposition of titanium, typical high-temperature molten salts are chloride [15–29], fluoride [30–34], and fluoride–chloride mixed molten salts [15,20,22,35–46]. Less common ones are iodide, bromide, and bromide–fluoride melts [19]. The electrochemical and chemical behaviors of titanium ions in molten salts have been also reported [47–82]. Table 1-1 summarizes the previous reports on electrodeposition of titanium in chloride melts. In a similar manner, Table 1-2, 1-3, and 1-4 summarize the previous reports on “fluoride”, “bromide, iodide, iodide–fluoride”, and “fluoride–chloride” melts, respectively.

Table 1-1 Previous studies on the electrodeposition of Ti metal in chloride melts.

Molten salt	Ti source	Ti ion conc.	Temperature / K	Current density / mA cm ⁻²	Authors	Year	Ref.
NaCl	TiCl ₃ or TiCl ₂	5%	1023	1500, 2000	Ervin <i>et al.</i>	1959	[15]
NaCl	TiCl ₃ , Ti	5 wt% (TiCl ₂)	1123	20–400	Haarberg <i>et al.</i>	1993	[16]
CaCl ₂	TiCl ₄ , Ti	5 wt% (TiCl ₂)	1173	100–900	Kang <i>et al.</i>	2015	[17]
LiCl–KCl	TiCl ₄	0.1–1 mol m ⁻³	673–773	100–200	Alpert <i>et al.</i>	1957	[18]
LiCl–KCl	TiC	—	1023	2000	Ervin <i>et al.</i>	1959	[15]
LiCl–KCl	Ti	—	973	520	Fortin <i>et al.</i>	1959	[19]
LiCl–KCl	TiCl ₃ or Ti	12 wt% (TiCl ₃)	803–823	1000–3000	Menzies <i>et al.</i>	1959	[20]
LiCl–KCl	TiCl ₃ , Ti	—	773–973	–1.20 V (vs. Ag ⁺ /Ag)	Kuma <i>et al.</i>	1990	[21]
LiCl–KCl	TiCl ₃ , Ti	5 wt% (TiCl ₂)	723	20–400 or –100 mV (vs. Ti ref.)	Haarberg <i>et al.</i>	1993	[16]
LiCl–KCl	TiCl ₃ , Ti	0.55–0.92 mol% (TiCl ₃)	773	–1.00––1.70 V (vs. Ag ⁺ /Ag)	Takamura <i>et al.</i>	1996	[22]
LiCl–KCl	TiCl ₂	0.5–1.0 mol% (TiCl ₂)	700	80, 120 (i _p , Pulse)	Gussone and Hausmann	2011	[23]
NaCl–KCl	Ti	—	998	500	Fortin <i>et al.</i>	1959	[19]
NaCl–KCl	TiCl ₃ , TiCl ₄ or Ti	12 wt% (TiCl ₃)	973–1023	1000–3000	Menzies <i>et al.</i>	1959	[20]
NaCl–KCl	TiCl ₃ , Ti	5 wt% (TiCl ₂)	923	20–400	Haarberg <i>et al.</i>	1993	[16]
NaCl–KCl	TiCl ₄ , Ti	2.5–7.6 wt% (Ti(II))	1023	50–800	Ning <i>et al.</i>	2011	[24]
NaCl–KCl	TiCl ₄ , Ti	2.7–6.5%	1173–1223	200–800	Yuan <i>et al.</i>	2011	[25]
NaCl–KCl	TiCl ₂	1 mol% (TiCl ₂)	1073	1.30 V	Wang <i>et al.</i>	2015	[26]
NaCl–KCl	TiCl ₂	5–10 mol% (TiCl ₂)	973	200–263 (i _p , Pulse)	Kishimoto <i>et al.</i>	2020	[27]
NaCl–CsCl	TiCl ₃	2.0 wt% (TiCl ₃)	873	300	Song <i>et al.</i>	2016	[28]
KCl–SrCl ₂	TiCl ₄	0.1–1 mol m ⁻³	973–1173	100–200	Alpert <i>et al.</i>	1957	[18]
NaCl–KCl–MgCl ₂	TiCl ₂	5 mol% (TiCl ₂)	773	200–263 (i _p , Pulse)	Kishimoto <i>et al.</i>	2020	[27]
NaCl–KCl–MgCl ₂ –CaCl ₂ –BaCl ₂	TiCl ₂ , TiCl ₃	—	713–763	—	Tokumoto <i>et al.</i>	1975	[29]

Table 1-2 Previous studies on the electrodeposition of Ti metal in fluoride melts.

Molten salt	Ti source	Ti ion conc.	Temperature / K	Current density / mA cm ⁻²	Authors	Year	Ref.
NaF	K ₂ TiF ₆	5–30 mol% (K ₂ TiF ₆)	1173–1273	500–4000	Matiasovsky <i>et al.</i>	1972	[30]
K ₂ TiF ₆	—	—	1173–1273	500–4000	Matiasovsky <i>et al.</i>	1972	[30]
LiF–NaF–KF	K ₂ TiF ₆ , Ti	0.95–5.0 × 10 ⁻² mol/L (K ₃ TiF ₆)	873–1073	39–150	Lepinay <i>et al.</i>	1987	[31]
LiF–NaF–KF	K ₂ TiF ₆ , Ti	0.51–1.5 × 10 ⁻² mol/L (Ti(III))	873–973	34.5–50	Robin <i>et al.</i>	1987	[32]
LiF–NaF–KF	K ₂ TiF ₆ , Ti	0.51 × 10 ⁻² mol/L (Ti(III))	973	32	Robin	1998	[33]
LiF–NaF–KF	K ₂ TiF ₆ , Ti	2.2 wt% (Ti(III))	973–1173	18–60 or 50–150 (i _p , Pulse)	Robin and Ribeiro	2000	[34]

Table 1-3 Previous studies on the electrodeposition of Ti metal in bromide, iodide, and iodide–fluoride melts.

Molten salt	Ti source	Ti ion conc.	Temperature / K	Current density / mA cm ⁻²	Authors	Year	Ref.
NaBr–KBr	Ti	—	998	1000	Fortin <i>et al.</i>	1959	[19]
NaI–KI	TiI ₄ , Ti	2–5 wt% (TiI ₄)	998–1048	400–1000	Fortin <i>et al.</i>	1959	[19]
KF–KI	K ₂ TiF ₆ , or Ti	2 wt% (K ₂ TiF ₆)	998–1023	400–700	Fortin <i>et al.</i>	1959	[19]

Table 1-4 Previous studies on the electrodeposition of Ti metal in fluoride–chloride mixed melts.

Molten salt	Ti source	Ti ion conc.	Temperature / K	Current density / mA cm ⁻²	Authors	Year	Ref.
NaCl	K ₂ TiF ₆	15–25 mol% (K ₂ TiF ₆)	988–1073	57–750	Steinberg <i>et al.</i>	1955	[35]
NaCl	K ₂ TiF ₆	5–25 mol% (K ₂ TiF ₆)	1123–1223	81–485	Sibert and Steinberg	1955	[36]
NaCl	K ₂ TiF ₆ or Na ₂ TiF ₆	—	1053–1093	—	Wurm <i>et al.</i>	1957	[37]
NaCl	K ₂ TiF ₆ , Ti or TiC	2% (Ti(IV))	1023	2000–2500	Ervin <i>et al.</i>	1959	[15]
LiCl–KCl	K ₂ TiF ₆ , Ti	11 wt% (K ₂ TiF ₆)	773	1000–3000	Menzies <i>et al.</i>	1959	[20]
NaCl–KCl	K ₂ TiF ₆ or Na ₂ TiF ₆	—	943–973	—	Wurm <i>et al.</i>	1957	[37]
NaCl–KCl	K ₂ TiF ₆ , Ti	17 wt% (K ₂ TiF ₆)	973–1123	500–1000 (<i>i</i> _p , Pulse)	Wei <i>et al.</i>	1993	[38]
NaCl–KCl	K ₂ TiF ₆ , Ti	10 wt% (K ₂ TiF ₆)	1023	800	Ene and Zuca	1995	[39]
NaCl–KCl	K ₂ TiF ₆ , Ti	12 wt% (K ₂ TiF ₆)	1023	1000–3000	Menzies <i>et al.</i>	1959	[20]
LiCl–NaCl–KCl–	K ₂ TiF ₆ , Ti	2 mol% (K ₂ TiF ₆)	773–923	–1.35 V––1.65 V (vs. Ag ⁺ /Ag) (<i>E</i> _p , Pulse)	Wei <i>et al.</i>	1993	[40]
LiCl–NaCl–KCl–	K ₂ TiF ₆ , Ti	2 mol% (K ₂ TiF ₆)	723–923	50–300 (<i>i</i> _p , Pulse)	Wei <i>et al.</i>	1994	[41]
LiCl–NaCl–KCl–	K ₂ TiF ₆ , Ti	2 mol% (K ₂ TiF ₆)	723–923	50–300 (<i>i</i> _p , Pulse)	Wei <i>et al.</i>	1994	[42]
LiCl–NaCl–KCl–	K ₂ TiF ₆ , Ti	2 mol% (K ₂ TiF ₆)	773–923	200 or 450 (<i>i</i> _p , Pulse)	Wei <i>et al.</i>	1994	[43]
LiCl–KCl–LiF	TiCl ₃ , Ti	—	773	–1.48, –1.38 V (vs. Ag/Ag ⁺)	Takamura <i>et al.</i>	1996	[22]
NaCl–KCl–NaF	K ₂ TiF ₆ , Ti	0.21–0.3 mol/L (Ti(III))	973	–2.06, –1.635 V (vs. Pt/Pt ²⁺) or Pulse current	Barner <i>et al.</i>	2005	[44]
NaCl–KCl–NaF	TiCl ₄	1 mol% TiCl ₄	1023	300–500	Zhu <i>et al.</i>	2017	[45]
NaCl–KCl–NaF	TiCl ₃	2.5 wt% (Ti(III))	1023–1123	25–80 or 75–175 (<i>i</i> _p , Pulse)	Malyshev and Shakhnin	2014	[46]

When chloride melts are used, in many cases, it is difficult to obtain smooth titanium film due to the dendritic or uneven titanium deposition. For example, Fig. 1-6 shows the electrodeposits obtained in (a) LiCl–KCl–TiCl₂ melt at 723 K [16] and (b) CaCl₂–TiCl₂ melt at 1173 K [17]. In the chloride melts, there are three oxidation states of titanium ions: Ti(IV), Ti(III), and Ti(II). Thus, electrodeposition of titanium occurs in one step from Ti(II), two steps from Ti(III), and three steps from Ti(IV) [15–29, 47–62].



In exceptional cases, it was reported that electrodeposition proceeds without forming Ti(II) in LiCl–CsCl melt at 673–793 K [59] and in CsCl melt at 1023 K [73].

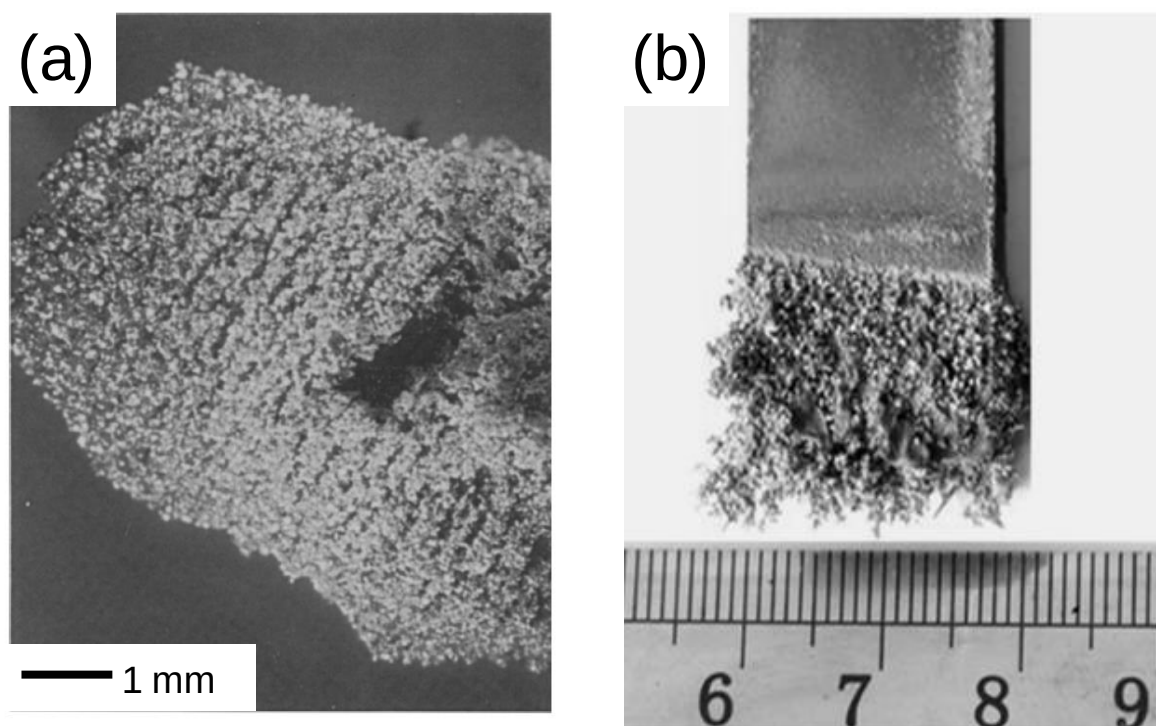


Fig. 1-6 Optical images of the samples obtained in (a) molten LiCl–KCl–TiCl₂ at 723 K [16] and (b) molten CaCl₂–TiCl₂ at 1173 K [17].



Takamura *et al.* reported that only *ca.* 0.2 mol% of Ti(II) ions were dissolved into the molten salt when TiCl₃ was added to LiCl–KCl at 773 K and equalized with sponge titanium [76]. Such a low solubility of Ti(II) ions is probably one of the major reasons that smooth titanium film is difficult to obtain in chloride melts. On the other hand, Gussone and Hausmann reported that comparatively smooth film was obtained by using pulse current electrolysis in LiCl–KCl–TiCl₂ [23]. Kishimoto *et al.* also obtained titanium films with smooth surface by pulse current electrolysis in NaCl–KCl molten salt at 973 K and in NaCl–KCl–MgCl₂ molten salt at 773 K, with the addition of 5–10 mol% TiCl₂ [27]. Tokumoto *et al.* reported that relatively smooth and thick film was obtained by stirring the melt in NaCl–KCl–MgCl₂–CaCl₂–BaCl₂ at 713–763 K [29]. These reports suggest that electrodeposition of smooth titanium film is possible by using molten salts with high solubility of Ti(II) ions or by promoting the diffusion of Ti(II) ions to avoid diffusion-limited conditions.

In the case of fluoride molten salts, Matiasovsky *et al.* reported that relatively compact titanium films with smooth surface were obtained by using K₂TiF₆ and NaF–K₂TiF₆ molten salts at 1173–1273 K [30]. Titanium films with compact and smooth surface were electrodeposited in LiF–NaF–KF at 873–1073 K by Lepinay *et al.* [31] and at 873–1173 K by Robin *et al.* [32–34]. According to the surface and cross-sectional SEM images of the titanium film reported by Robin *et al.*, as shown in Fig. 1-7 [32], compact and smooth films were electrodeposited. The reduction behavior of titanium ions in LiF–NaF–KF and LiF–KF has also been investigated [30–34,47–49,63–65]. The existence of Ti(II) ions has not been observed in the molten fluorides. Electrodeposition of titanium occurs in two steps from Ti(IV) ions and in one step from Ti (III) ions.

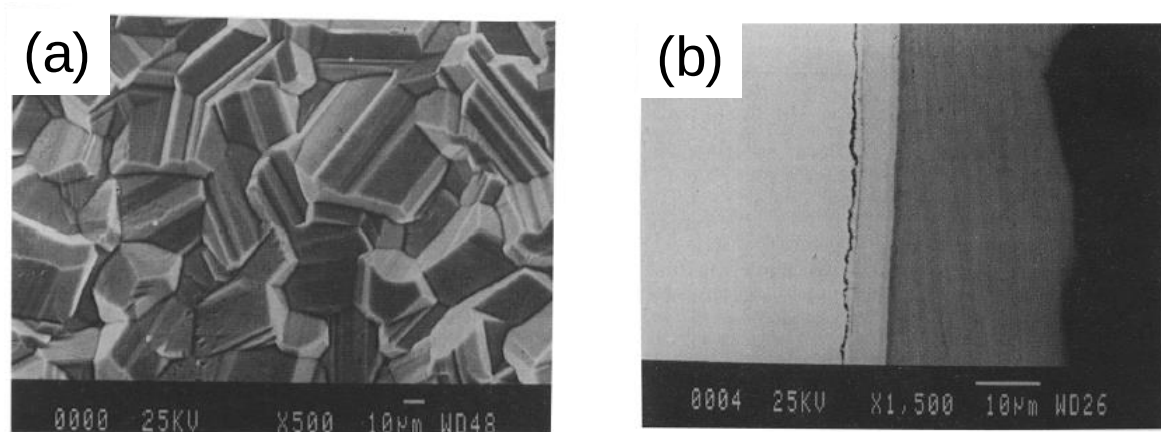


Fig. 1-7 (a) Surface and (b) cross-sectional SEM images of the sample obtained in molten KF–LiF–NaF–K₃TiF₆ at 973 K [32].



Although compact and smooth titanium films can be obtained from fluoride melts, high corrosivity of the melts and difficulty of removing solidified salt are problems.

Electrodeposition using fluoride–chloride mixed molten salt has also been investigated. Relatively smooth titanium films were obtained in LiCl–NaCl–KCl–K₂TiF₆ or LiCl–KCl–K₂TiF₆ at 723–1123 K by Oki *et al.* [38,40–43] and in NaCl–KCl–K₂TiF₆ at 1023 K by Ene and Zuca [39]. Takamura *et al.* reported that the addition of LiF to LiCl–KCl melt improves the morphology of the deposit at 773 K [22]. Barner *et al.* and Malyshev *et al.* obtained that relatively smooth titanium films in NaCl–KCl–NaF at 973 K [44] and in NaCl–KCl–NaF–TiCl₃ at 1023–1073 K [46], respectively. Chen *et al.* investigated the effect of adding fluoride ions to chloride molten salt. When over 10 wt% of KF was added to NaCl–KCl–3 wt% K₂TiF₆ at 923 K, the reaction of Ti(III) to Ti(II) disappears, and the existing state of titanium ions is close to that in fluoride melts [67]. Song *et al.* also investigated the effect of fluoride ions by adding KF to NaCl–KCl–TiCl₃ at 1023 K [72]. As a result, when [F]/[Ti] is increasing and close to 6, the overvoltage becomes high and a

good deposit with a small grain size is obtained. These reports show the high fluoride-ion concentration is advantageous for depositing compact and smooth titanium films. In the case of iodide molten salts, good titanium film was obtained when the fluoride salt was mixed [19].

From the previous reports, when fluoride salts or fluoride–chloride molten salts are used, electrodeposition of compact and smooth titanium films becomes easier. In these melts, Ti(II) ions do not exist and the solubility of Ti(III) ions is relatively high. Therefore, it is considered that Ti(III) ions are less likely to be diffusion-limited during electrodeposition. Moreover, relatively smooth film was obtained when sufficient Ti(III) ions were provided by the following comproportionation reaction.



1.5 Purpose of This Study and Selection of Molten Salt

As described in the previous section, a large number of researchers have reported the electrodeposition of metallic titanium in high-temperature molten salts. From the perspective of corrosiveness of molten salt, removal of solidified salt and obtaining smooth titanium films, fluoride–chloride mixed molten salts are promising. Therefore, there have been several studies on the role of anions in fluoride–chloride mixed molten salts. Although there were some reports on the effects of fluoride ion concentration in fluoride–chloride mixed molten salts, the used molten salts in all reports contained multiple kinds of cations. Thus, the effects of cations and anions cannot be separated in the past literature. From this background, the author focused on fluoride–chloride mixed molten salts consisting of single cations. By using such molten salts, the effects of cations and anions are expected to be investigated individually. Specifically, KF–KCl and LiF–LiCl were selected as the molten salts in this study. The reasons for the selection are explained below.

1.5.1 KF–KCl Molten Salt

As mentioned in the previous section, compact and smooth titanium films can be obtained in fluoride or fluoride-based melts. However, one of the major problems of using these melts is the difficulty in removing the solidified salts from the deposited Ti films by water washing, because of the low solubility of fluoride salts as shown in Table 1-5 [83]. This problem could be critical for practical use. On the other hand, KF exhibits an exceptionally high solubility in water among alkaline and alkaline earth fluoride salts. Therefore, in this study, KF salt was selected as one of the main constituent salts.

However, the use of single KF molten salt is problematic owing to its high melting point (1131 K). In general, the utilization of binary or ternary molten salts is an effective way to lower the melting points. Since fluoride salts other than KF have low solubility in water, chloride salts are candidates for the mixing salt. If one of LiCl, NaCl, MgCl₂, and CaCl₂ is mixed with KF, a water-insoluble fluoride salt is formed. For example, if LiCl is mixed with KF, LiF is produced according to the reaction,

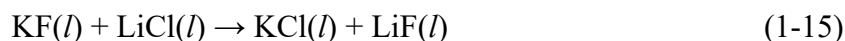


Table 1-5 Solubilities in water at 298 K for representative alkali halides and alkaline earth halides [83].

Alkali fluoride Alkaline earth fluoride	Solubility / g (100g-H ₂ O) ⁻¹	Alkali chloride Alkaline earth chloride	Solubility / g (100g-H ₂ O) ⁻¹
LiF	0.13	LiCl	84.5
NaF	4.1	NaCl	36.0
KF	101.6	KCl	35.5
MgF ₂	0.013	MgCl ₂	56.0
CaF ₂	0.0016	CaCl ₂	81.3

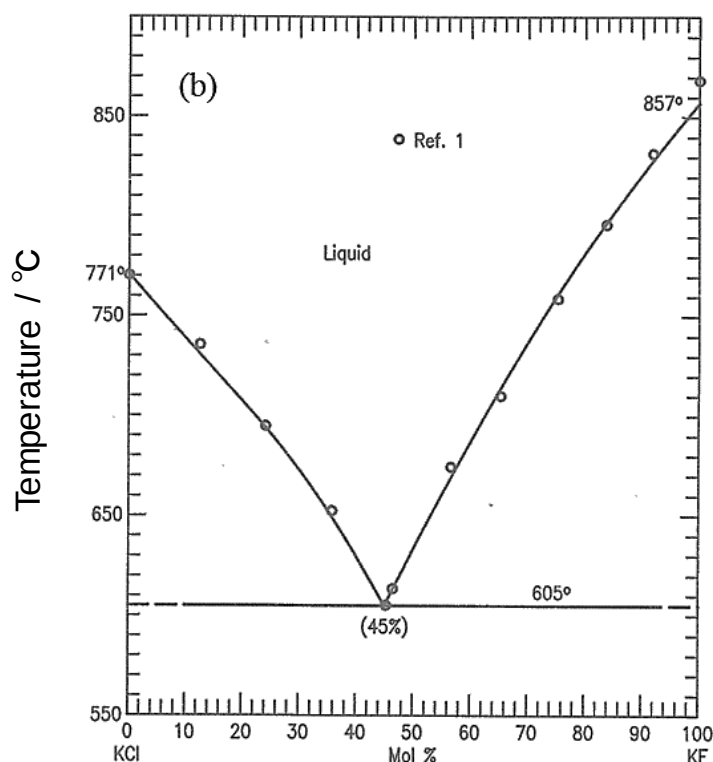


Fig. 1-8 A phase diagram for the KF–KCl system [84].

Therefore, KCl was selected as the other constituent salt. Since KCl also has high a solubility in water, it is possible to lower the melting point without losing the water solubility. Fig. 1-8 shows a phase diagram for the KF–KCl system, in which melting point is 878 K at the eutectic composition, KF:KCl = 45:55 mol% [84].

1.5.2 LiF–LiCl Molten Salt

So far, most of the previous studies on the electrodeposition of titanium and the electrochemical behavior of titanium ions in the fluoride–chloride mixed molten salts have been performed in, molten salts consisting of multi alkali-cations such as LiCl–KCl–NaF. The kinds of alkali-cations are important factor for the electrochemical behavior of titanium ions because the cations would influence the fluoro-acidity of molten salts that is defined by the free F^- content in the melt. However, there has been no study focusing on the cations in the fluoride–chloride mixed molten salts. Therefore, in this study, LiF–LiCl was selected for comparison with KF–KCl.

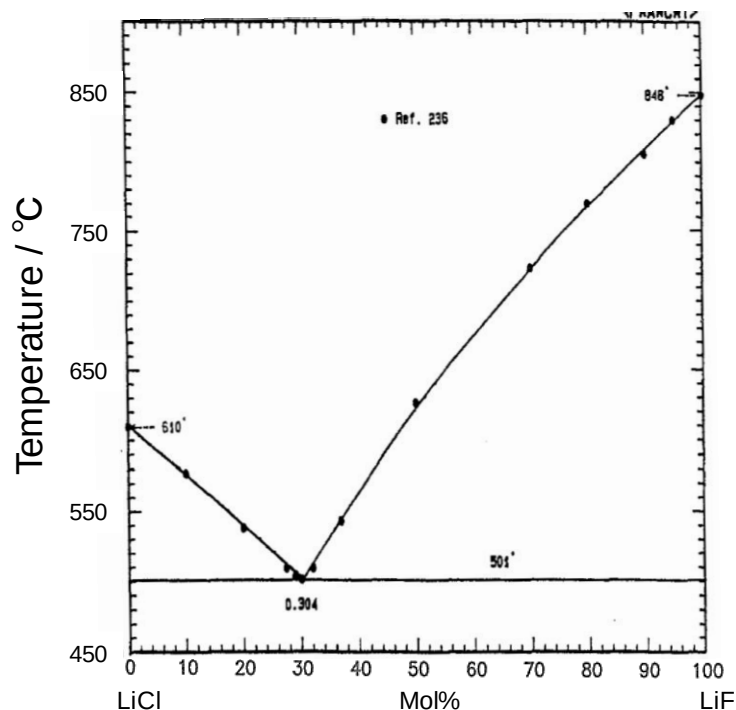


Fig. 1-9 A phase diagram for the LiF–LiCl system [85].

According to the phase diagram of the LiF–LiCl shown in Fig. 1-9, the eutectic temperature of LiF–LiCl (LiF:LiCl = 30:70 mol%) is 774 K, which is lower than that of the KF–KCl system [85]. When LiF–LiCl is used at the same molar ratio of anions as the eutectic KF–KCl (LiF:LiCl = 45:55 mol%), the melting point is approximately 873 K. Then, the effect of cations can be investigated at the same temperature of 923 K in LiF–LiCl and KF–KCl with the same anion ratio ($F^-:Cl^- = 45:55$ mol%).

1.6 Outline of This Study

For the widespread use of titanium metal, electrodeposition of metallic titanium films and the electrochemical behavior of titanium ions in fluoride–chloride mixed molten salts consisting of single cations are investigated in this study. Also, the effects of cations on the electrochemical behavior of titanium ions in fluoride–chloride mixed molten salts are discussed.

In this study, Ti(III) ions are prepared by the comproportionation reaction (Reaction 1-14) because compact and relatively smooth titanium films were electrodeposited from Ti(III) ions in

fluoride or fluoride–chloride melts in the literatures [31–34,38–43,46].

In Chapter 2, as an initial study for the KF–KCl molten salt, cyclic voltammetry is conducted to investigate the electrochemical behavior of titanium ions after adding of K_2TiF_6 (0.10 mol%) and an excess amount of sponge titanium at 923 K. Electrodeposition of titanium is also conducted in the same melt. The surface and cross-section of the obtained titanium are observed by scanning electron microscopy (SEM) and analyzed by energy dispersive X-ray spectroscopy (EDX) and X-ray diffractometry (XRD). The preferential crystal orientations of the electrodeposited titanium metal films are also investigated by XRD.

In Chapter 3, the electrochemical behavior of titanium ions is investigated in more detail in KF–KCl eutectic molten salt after the addition of K_2TiF_6 (0.50 mol%) and sponge titanium (0.33 mol%) at 923 K. The electrochemical reaction of titanium ions is analyzed using cyclic voltammetry and square wave voltammetry. From the results, the oxidation state of titanium ions in the melt and the formal redox potential of the reaction are evaluated. Furthermore, the diffusion coefficient of Ti(III) ions is estimated by cyclic voltammetry and chronoamperometry.

In Chapter 4, the optimum electrolysis conditions for electrodepositing titanium films with compact and smooth surface are investigated in KF–KCl molten salt at 923 K. The solubility of Ti(III) ions is determined by cyclic voltammetry and the inductively coupled plasma atomic emission spectroscopy (ICP-AES). Then, electrodeposition is conducted at various Ti(III) ion concentrations and cathodic current densities. The surface and cross-section of the electrodeposited titanium are observed by SEM to discuss the influence of the electrolysis conditions on the morphology. Moreover, a corrosion resistance test is conducted for the electrodeposited titanium film on a nickel plate by linear sweep voltammetry in artificial seawater.

In Chapter 5, LiF–LiCl molten salt having the same anion ratio as the eutectic KF–KCl molten salt ($\text{F}^-:\text{Cl}^- = 45:55$ mol%) is used. The electrochemical behavior of Ti(III) ions is investigated at 923 K as with Chapter 4. By comparing the results of LiF–LiCl and KF–KCl systems, the effect of alkali cations on the electrochemical behavior of Ti(III) ions is discussed.

In Chapter 6, the effects of temperature on the electrochemical behavior of Ti(III) ions and electrodeposition of titanium film are investigated in the eutectic LiF–LiCl melt in the temperature range of 823–973 K. The activation energy of titanium ion diffusion is calculated from the temperature dependence of the diffusion coefficient. Electrodeposition of titanium is conducted at each temperature, and the effects of bath temperature on crystal growth and surface smoothness of titanium films are investigated by SEM observation.

Finally, Chapter 7 summarizes the previous chapters. In particular, discussion is made on the effect of cations on the electrochemical behavior of Ti(III) ions. Moreover, the relationship between electrolysis conditions and the morphology of electrodeposited titanium films in fluoride–chloride mixed molten salts consisting of single cations are considered to obtain compact and smooth films.

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Chapter 2

Electrodeposition of Titanium in Water-Soluble KF–KCl Molten Salt

2.1 Introduction

In this chapter, as an initial study of electrodeposition of Ti in fluoride–chloride mixed molten salts consisting of single cations, investigations are conducted using KF–KCl eutectic melt (KF:KCl = 45:55 mol%) at 923 K. Firstly, Ti(III) ions are prepared in-situ by adding K_2TiF_6 and an excess amount of sponge Ti into the melt. Secondly, the electrochemical behavior of Ti(III) ions is studied by cyclic voltammetry. Finally, electrodeposition samples are prepared by galvanostatic electrolysis at several current densities; they are analyzed by SEM, EDX, and XRD to find the optimum current density for obtaining adherent, compact, and smooth Ti films.

2.2 Experiment

A schematic representation of the experimental apparatus is shown in Fig. 2-1. Reagent grade KF (FUJIFILM Wako Pure Chemical Co., Ltd., > 99.0%) and KCl (FUJIFILM Wako Pure Chemical Co., Ltd., > 99.5%) were mixed to achieve the eutectic composition (molar ratio of KF:KCl = 45:55, melting point = 878 K [1], 400 g) and loaded in a graphite crucible (Toyo Tanso Co., Ltd., outer diameter: 90 mm, inner diameter: 80 mm, and height: 120 mm) or nickel crucible (Chiyoda Industry Co., Ltd., outer diameter: 98 mm, inner diameter: 96 mm, and height: 102 mm). The mixture in the crucible was first dried under vacuum at 453 K for more than 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. After the blank measurements in KF–KCl, 0.10 mol% K_2TiF_6 (Morita Chemical Industry Co., Ltd., > 97.5%) and an excess amount (10 g) of sponge Ti (FUJIFILM Wako Pure Chemical Co., Ltd., > 99%) were added to the melt. Here, 10 g of sponge Ti is approximately 100 times the amount necessary to generate Ti(III) ions from 0.10 mol% K_2TiF_6 according to Reaction 1-14.

Electrochemical measurements and galvanostatic electrolysis were conducted using a three-electrode system (Hokuto Denko Corp., HZ-3000). The working electrodes were a Ni plate (Nilaco Corp., 5 mm × 10 mm, thickness: 0.1 mm, > 99%), a Ni flag (Nilaco Corp., diameter: 2.0 mm,

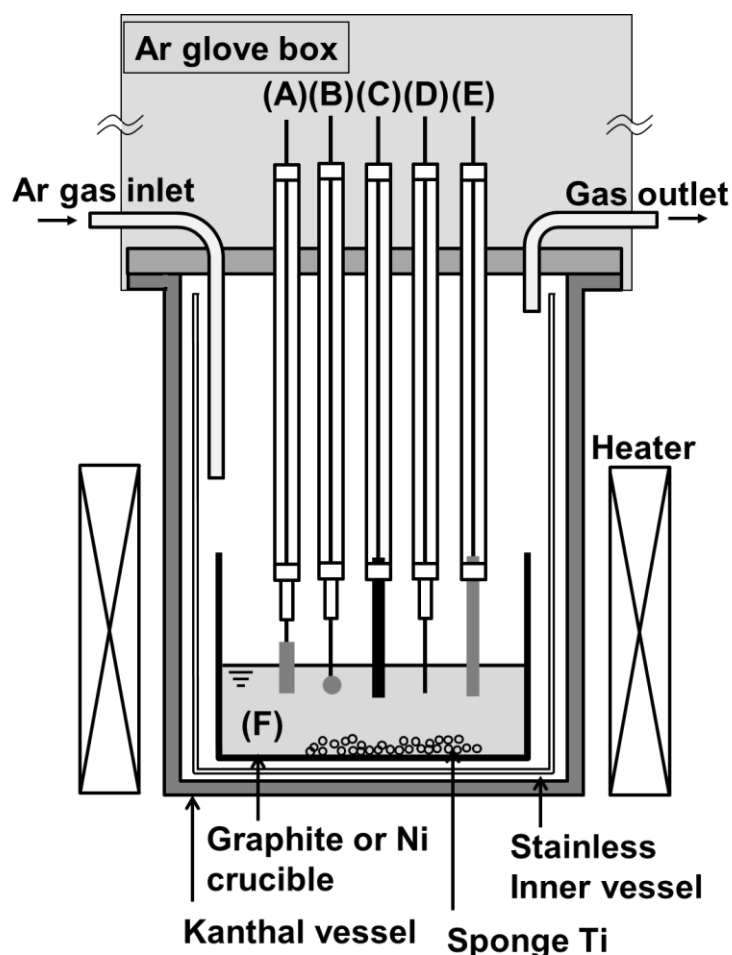


Fig. 2-1 A schematic representation of the experimental apparatus: (A) Ni plate electrode, (B) Ni flag electrode, (C) glass-like carbon rod electrode, (D) Pt and Mo wire electrodes, (E) Ti rod electrode, and (F) molten KF–KCl.

thickness: 0.1 mm, 99.98%), and a glass-like carbon (G.C.) rod (Tokai Carbon Co., Ltd., diameter: 3.0 mm). The structure of the Ni flag electrode was reported in a previous paper [2]. In order to remove the oxide film before usage, a Ni plate for electrodeposition was electropolished in 50 wt% sulfuric acid at 200 mA cm^{-2} 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 and dried. A Ti rod (Nilaco Corp., diameter: 3.0 mm, 99.5%) was used as the counter electrode, and a Pt wire (Nilaco Corp., diameter: 1.0 mm, > 99.98%) was employed as a quasi-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 wire (Nilaco Corp., diameter: 1.0 mm, 99.95%). 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).

2.3 Results and Discussion

2.3.1 Cyclic Voltammetry

Fig. 2-2(a) shows the cyclic voltammograms from the open-circuit potential to the positive direction measured at a glass-like carbon electrode before and after the addition of 0.10 mol% K_2TiF_6 and an excess amount of sponge Ti at 923 K. The anodic currents sharply increase at 3.6 V (vs. K^+/K) (current (b)) regardless of the addition. The theoretical decomposition voltage of $\text{KCl}(l)$ is calculated to be 3.63 V from the standard Gibbs energy of formation ($-345.5 \text{ kJ mol}^{-1}$) [3],

assuming that the activity of LiCl is 0.55. Thus, it is conceivable that the anodic currents above 3.6 V correspond to the generation of Cl_2 gas.

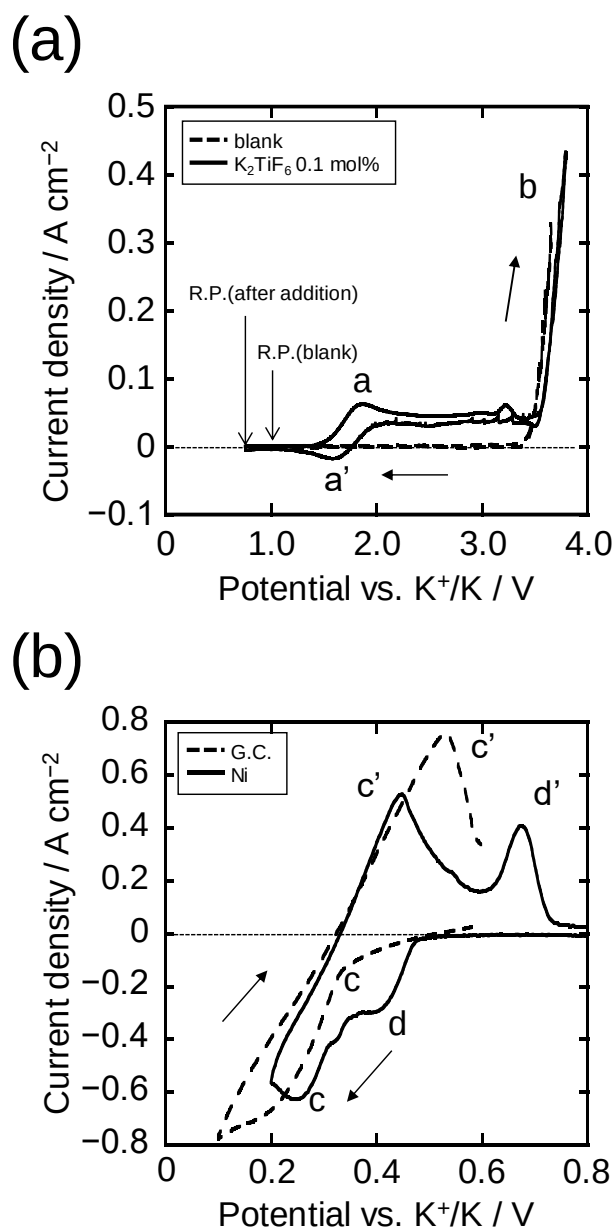


Fig. 2-2 Cyclic voltammograms in molten KF–KCl at 923 K obtained at a scan rate of 0.10 Vs^{-1} . (a) Positive potential region was measured at a glass-like carbon rod electrode before (dashed curve) and after (solid curve) the addition of 0.10 mol% K_2TiF_6 and an excess amount of sponge Ti. (b) Negative potential region was measured at a glass-like carbon rod electrode (dashed curve) and a Ni flag electrode (solid curve) after the addition of 0.10 mol% K_2TiF_6 and an excess amount of sponge Ti.



After the addition of K_2TiF_6 and sponge Ti, anodic currents are also observed from 1.5 V on the positive scan (current (a)), which is explained by the oxidation of Ti(III) to Ti(IV).

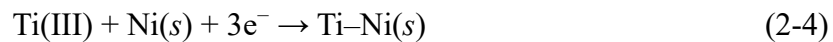


In the present experiment, rest potential (R.P.) was observed at approximately 0.7 V. Since this value is much more negative than the redox potential of Ti(IV)/Ti(III), most of the Ti ions exist as Ti(III) in the melt.

Fig. 2-2(b) shows the cyclic voltammograms measured at the glass-like carbon from 0.6 V to the negative direction (dashed curve) and Ni flag electrodes from 0.8 V to the negative direction (solid curve) after the addition of K_2TiF_6 and sponge Ti. For both electrodes, cathodic currents flow from approximately 0.3 V (current (c)). After the reversal of scanning direction, the corresponding anodic currents are also observed. From this result, it is expected that Ti metal is deposited from Ti(III) ions at potentials more negative than 0.3 V.



At the nickel flag electrode in Fig. 2-2(b), reduction currents are also observed from 0.5 V (current (d)). From the phase diagram of the Ti–Ni system in Fig. 2-3, three intermetallic compounds, TiNi_3 , TiNi , and Ti_2Ni exist at 923 K [4]. Thus, the observed currents (d) are likely to be associated with the formation of these Ti–Ni alloys.



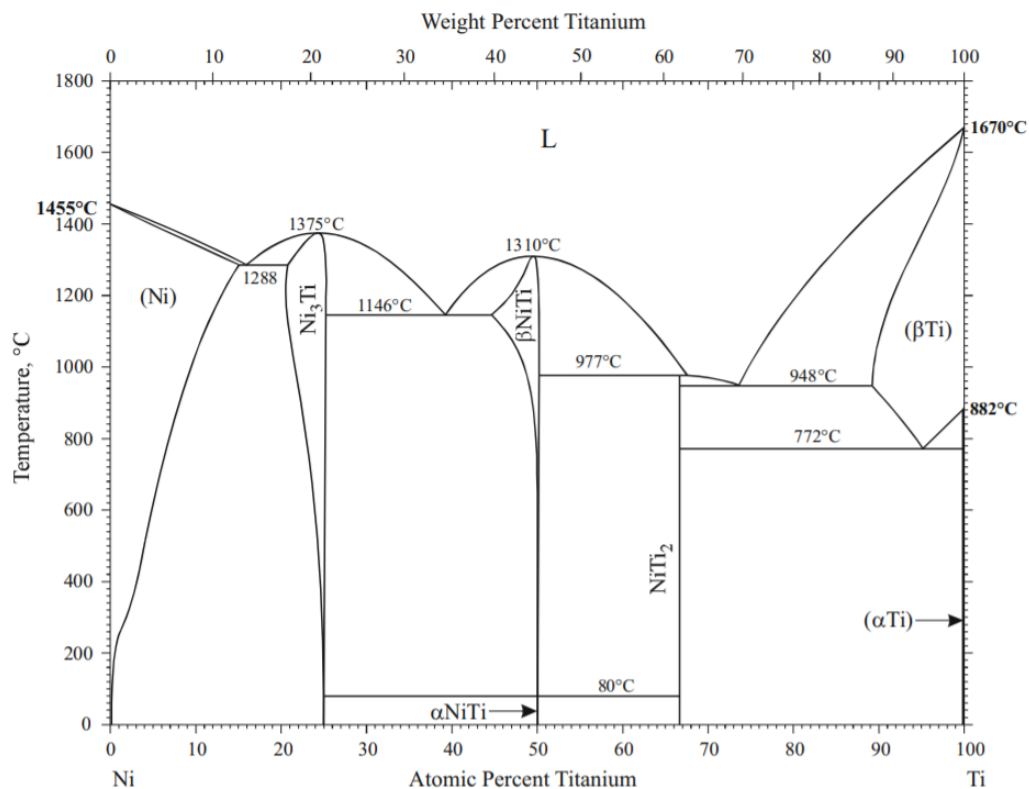
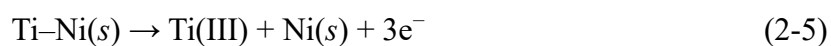


Fig. 2-3 A binary phase diagram for the Ti–Ni system [4].

The corresponding anodic currents (d') are then explained by the dissolution of Ti from the alloys.



2.3.2 Galvanostatic Electrolysis

To prepare the deposition samples, galvanostatic electrolysis was conducted using the Ni plate electrodes at 923 K. Fig. 2-4 shows the surface and cross-sectional SEM images of samples. The cathodic current densities were (a) 25, (b) 50, (c) 100, and (d) 150 mA cm⁻². The total quantity of electricity was fixed at 150 C cm⁻².

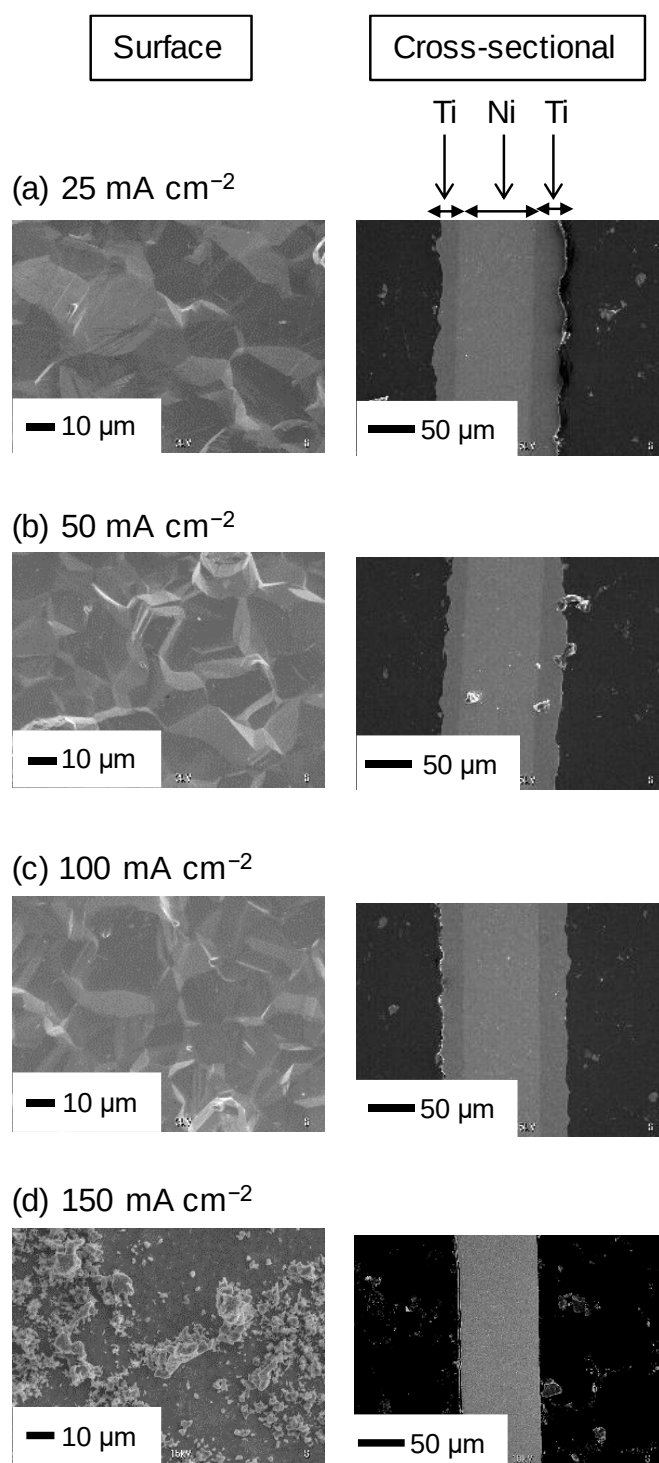


Fig. 2-4 Surface and cross-sectional SEM images of the samples obtained by galvanostatic electrolysis of Ni plate electrodes in molten KF-KCl after the addition of K_2TiF_6 (0.10 mol%) and an excess amount of sponge Ti at 923 K. Cathodic current density and time: (a) 25 mA cm^{-2} for 100 min, (b) 50 mA cm^{-2} for 50 min, (c) 100 mA cm^{-2} for 25 min, and (d) 150 mA cm^{-2} for 16.7 min.

As seen from the surface SEM images, the films prepared under conditions (a), (b), and (c) were densely packed with compact crystal grains. From the cross-sectional SEM images at the center of the sample plates, the films had smooth surfaces and thicknesses around 20 μm . EDX analysis revealed only Ti, implying 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 dissolved by water washing.

As seen in the XRD patterns (Fig. 2-5), deposition of crystalline titanium metal (α -Ti: hexagonal close-packed structure) is confirmed for samples (a), (b), and (c). Thus, the reduction currents approximately at 0.3 V were due to the deposition of Ti metal. The current efficiencies for

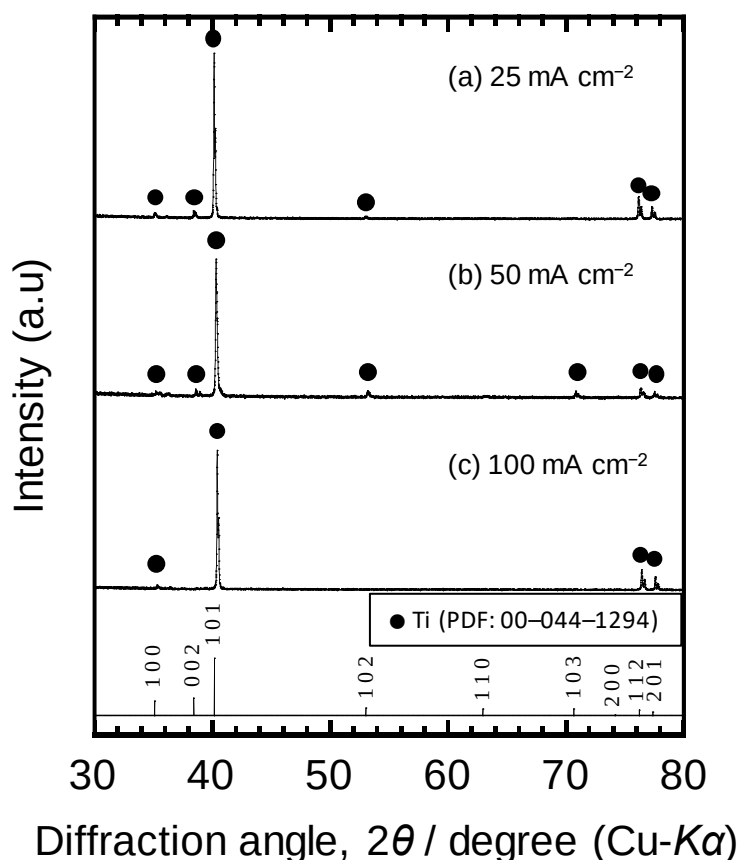


Fig. 2-5 XRD patterns of the samples obtained by galvanostatic electrolysis of Ni plate electrodes in molten KF-KCl after the addition of K_2TiF_6 (0.10 mol%) and an excess amount of sponge Ti at 923 K. Cathodic current density and time: (a) 25 mA cm^{-2} for 100 min, (b) 50 mA cm^{-2} for 50 min, and (c) 100 mA cm^{-2} for 25 min.

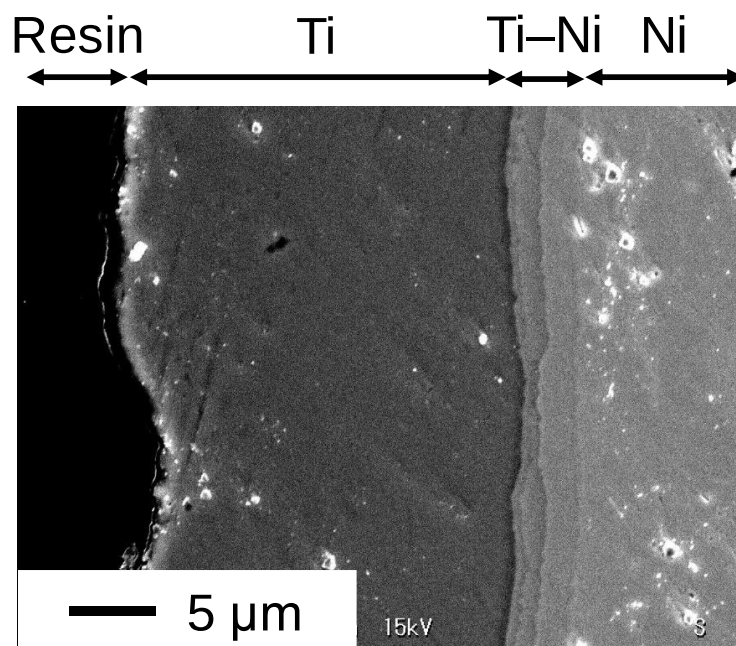


Fig. 2-6 A cross-sectional SEM image of the sample obtained by galvanostatic electrolysis of a Ni plate electrode in molten KF–KCl after the addition of K_2TiF_6 (0.10 mol%) and an excess amount of sponge Ti at 923 K. Cathodic current density and time: 50 mA cm^{-2} for 50 min.

Ti deposition calculated from the weight increase were 87%, 77%, and 81% at 25, 50, and 100 mA cm^{-2} , respectively. Under the assumption of a 3-electron reaction, the theoretical thickness of the Ti layer is calculated to be $55 \mu\text{m}$, which is much higher than the observed thickness about $20 \mu\text{m}$. This could be attributed to the uneven distribution of current – high current densities at the edges and low current densities at the center.

Moreover, as shown in the high magnification SEM image of sample (b) (Fig. 2-6), Ti–Ni alloy layers with $3 \mu\text{m}$ thickness are observed at the interface between a deposited Ti film and a Ni substrate. Meanwhile, Ti films were not obtained at the highest current density of (d) 150 mA cm^{-2} . This is explained by the formation of a K metal fog at high current density and the detachment of the metal deposit. A similar phenomenon was observed for the deposition of Si in the KF–KCl molten salt [5].

The preferred crystal orientation of the obtained Ti films was evaluated from the peak

intensities in the XRD patterns. Table 2-1 lists the orientation index, α_{hkl} , calculated for samples (a), (b), and (c) using the equation proposed by Willson *et al* [6].

$$\alpha_{hkl} = \frac{I_{hkl}(\text{sample}) / \sum I(\text{sample})}{I_{hkl}(\text{PDF}) / \sum I(\text{PDF})} \quad (2-6)$$

Here, $I_{hkl}(\text{sample})$ and $I_{hkl}(\text{PDF})$ indicate the peak intensity of hkl diffraction for the deposits and PDF data (# 00–044–1294), respectively. The values of $\sum I(\text{sample})$ and $\sum I(\text{PDF})$ indicate the sum of peak intensities for the all diffractions for the deposits and PDF data, respectively. As the result, α_{101} is higher than 1.8 for all the deposits, which demonstrates the high orientation to $\{101\}$ plane. Oki *et al.* reported that the Ti metal film deposited on nickel in KCl–NaCl–LiCl containing K_2TiF_6 at 923 K was highly orientated to $\{001\}$ plane [7]. They also reported that the orientation varied with temperature, electrolysis time, current density, and electrolysis method. Similarly, the preferred orientation might be influenced by the electrolysis conditions in the present case and will be reported in the future.

Table 2-1 Orientation index of the samples obtained by galvanostatic electrolysis of Ni plate electrodes in molten KF–KCl after the addition of K_2TiF_6 (0.10 mol%) and an excess amount of sponge Ti at 923 K. Cathodic current density and time: (a) 25 mA cm^{-2} for 100 min, (b) 50 mA cm^{-2} for 50 min, and (c) 100 mA cm^{-2} for 25 min.

Diffraction index, hkl	Diffraction angle, 2θ / degree (Cu-K α)	Orientation index, α_{hkl}		
		25 mA cm^{-2}	50 mA cm^{-2}	100 mA cm^{-2}
1 0 0	35.09	0.12	0.07	0.12
0 0 2	38.42	0.31	0.38	0.00
1 0 1	40.17	1.86	1.88	1.92
1 0 2	53.01	0.13	0.42	0.00
1 1 0	62.95	0.04	0.06	0.00
1 0 3	70.66	0.00	0.52	0.00
2 0 0	74.15	0.00	0.00	0.00
1 1 2	76.22	1.53	0.91	1.64
2 0 1	77.37	1.06	0.59	1.28

2.4 Conclusion

Electrodeposition of Ti 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 mol% K_2TiF_6 and an excess amount of sponge Ti, and the electrochemical behaviors were investigated by cyclic voltammetry. The oxidation of Ti(III) ions to Ti(IV) ions was observed from 1.5 V vs. K^+/K in the positive scan at a glass-like carbon electrode. Cathodic currents corresponding to the deposition of metallic Ti were observed at potentials more negative than 0.3 V. At the Ni electrode, cathodic currents due to the formation of Ti–Ni alloys also flowed from 0.5 V. The solidified salt was successfully removed by washing with water, and the deposits obtained by galvanostatic electrolysis were analyzed by surface and cross-sectional SEM, EDX, and XRD. The films deposited at current densities of 25 mA cm^{-2} had smooth surfaces and approximately 20 μm thickness. XRD analysis revealed that crystalline metallic Ti was deposited, and that the Ti films were highly orientated to {101} plane.

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Chapter 3

Electrochemical Behavior of Ti(III) Ions in KF–KCl Eutectic Molten Salt

3.1 Introduction

In the previous chapter, the electrodeposition of Ti films has been demonstrated for Ni substrates in KF–KCl eutectic melt at 923 K. Also, the electrochemical behavior of Ti(III) ions has been investigated using glass-like carbon and Ni electrodes. In the present chapter, the electrochemical behavior of Ti(III) ions is investigated in more detail to obtain fundamental data concerning the molten salt system. To prescribe the electrode area precisely, metal electrodes such as Mo and Pt are used as the working electrodes instead of a glass-like carbon electrode. The Mo electrode is used for investigating the cathodic reaction of Ti(III) ions because Mo hardly forms alloy with Ti. The Pt electrode is used for studying the anodic reaction as it has a wide potential window on the positive side. Cyclic voltammetry and square wave voltammetry are conducted to analyze the cathodic and the anodic reactions of Ti(III) ions. Furthermore, the diffusion coefficient of Ti(III) ions is evaluated using cyclic voltammetry and chronoamperometry.

3.2 Experiment

A preparation method of KF–KCl molten salt, an experimental apparatus, and analysis methods are almost the same as Chapter 2. Important and/or different points are described below.

Electrochemical measurements and galvanostatic electrolysis were conducted using a three-electrode method with an electrochemical measurement system (Hokuto Denko Corp., HZ-7000).

The working electrodes were Mo plate (Nilaco Corp., 5 mm × 10 mm, thickness: 0.1 mm, 99.95%), Mo flag (Nilaco Corp., diameter: 2.0 mm, thickness: 0.1 mm, 99.95%), and Pt flag (Nilaco Corp., diameter: 2.0 mm, thickness: 0.1 mm, 99.98%) electrodes. Prior to the experiments, the Mo and Pt electrodes were washed with ethanol and well dried. A Ti plate (Nilaco Corp., 5 mm × 10 mm, thickness: 0.1 mm, 99.5%) was used as the counter electrode. A Ti rod (Nilaco Corp., diameter: 3.0 mm, 99.5%) was employed as the reference electrode. In the blank measurement, a Pt wire (Nilaco Corp., diameter: 1.0 mm, 99.98%) was used as the quasi-reference electrode. The electrolyzed samples on the Mo plates were soaked in distilled water at 333 K for 10 min to remove the salt adhered on the deposits. A small portion of molten salt was sampled and dissolved in a 10 wt% HF aqueous solution (prepared from Tama Chemical Corp., AA-100 grade, 38 wt%). The solution was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Hitachi, Ltd., SPECTRO BLUE) to determine the Ti ion concentration in molten salt.

3.3 Results and Discussion

3.3.1 Reduction of Ti(III) Ions

3.3.1.1 Cyclic Voltammetry

Fig. 3-1 shows the cyclic voltammogram in the negative potential region obtained at a Mo flag electrode after the addition of 0.50 mol% of K_2TiF_6 and 0.33 mol% of sponge Ti at a temperature of 923 K and a scan rate of 0.50 V s^{-1} . As described in Chapter 2, Ti(III) ions were generated by comproportionation reaction (Reaction 1-14) and most of Ti ions exist as Ti(III) in the melt. For comparison, the voltammogram before the addition is also plotted. From approximately 0.4 V vs. K^+/K , cathodic current (A) is observed, which corresponds to electrodeposition of Ti metal. After reversing the scanning direction, anodic current (A') is also observed, which is due to anodic dissolution of Ti metal.

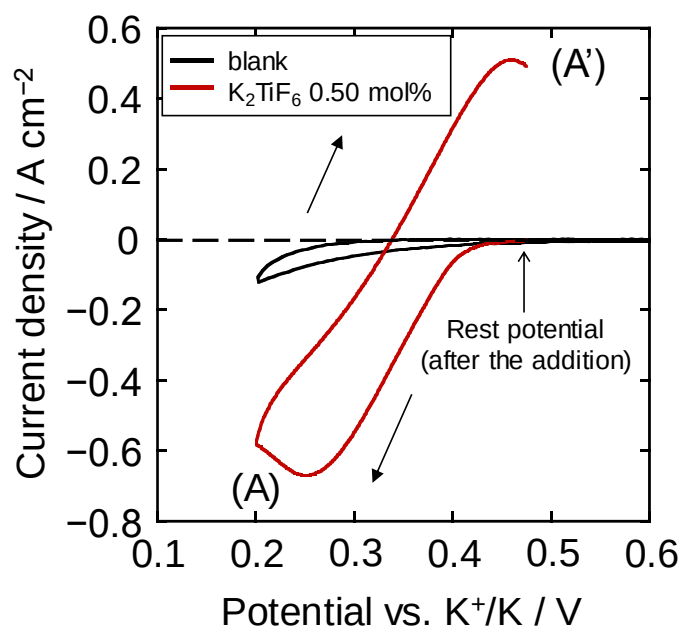


Fig. 3-1 Cyclic voltammograms at a Mo flag electrode in molten KF–KCl before and after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K. Scan rate: 0.50 V s^{-1} .

3.3.1.2 Galvanostatic Electrolysis, XRD, and SEM/EDX

To confirm that the cathodic current (A) corresponds to Ti metal deposition, galvanostatic electrolysis was conducted using a Mo plate electrode at a current density of -50 mA cm^{-2} for 20 min. Fig. 3-2 shows the potential transient curve during the galvanostatic electrolysis. The potential during the electrolysis is around 0.32 V, which indicates the progress of the cathodic reaction observed in the cyclic voltammogram. Fig. 3-3(a) shows the optical image of the sample after washing in water. The entirety of the substrate is covered with a deposit having metallic luster. Fig. 3-3(b) shows the XRD pattern of the sample, which clearly indicates the existence of metallic Ti. The surface and cross-sectional SEM images of the sample are shown in Fig. 3-4(a) and (b), respectively. The deposit is compact and composed of grains with diameters of approximately $10 \mu\text{m}$. EDX analysis of the deposit detected only Ti. The cross-sectional SEM image confirms that adherent and smooth films with a thickness of $20 \mu\text{m}$ are electrodeposited on the Mo substrate. From these results, the cathodic wave in the cyclic voltammogram is confirmed to the reduction of Ti(III) ions to metallic Ti.

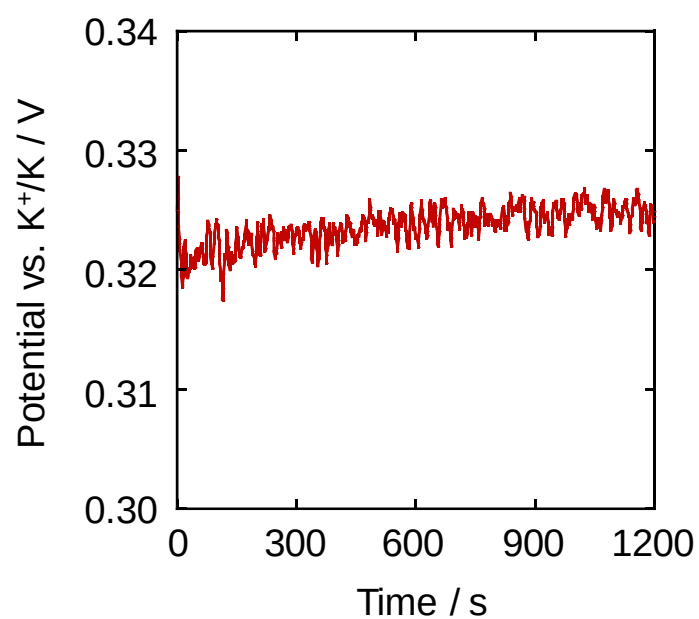


Fig. 3-2 A potential transient curve during the galvanostatic electrolysis at a Mo plate electrode at -50 mA cm^{-2} for 20 min in KF–KCl after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

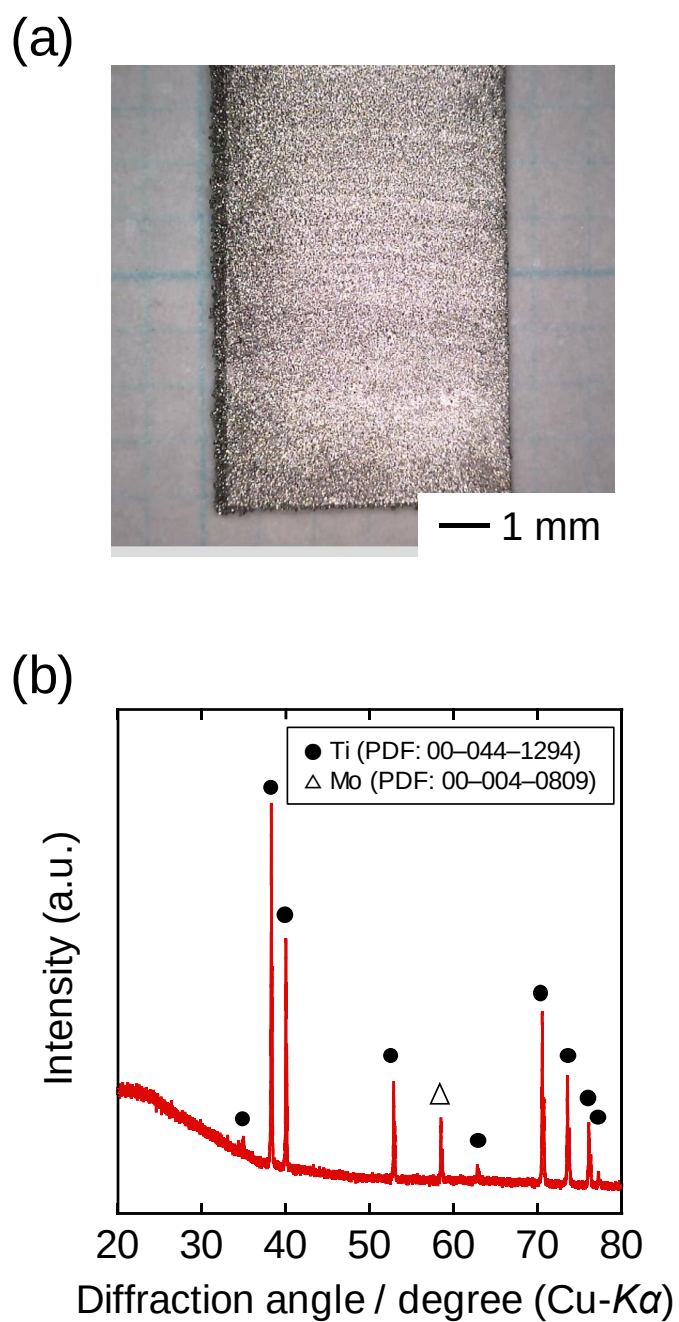
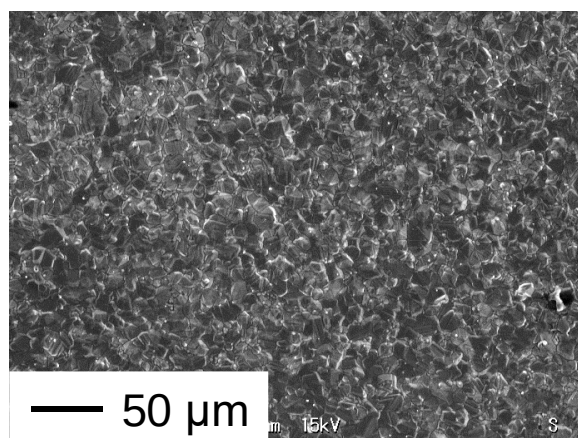


Fig. 3-3 (a) An optical image and (b) an XRD pattern of the sample obtained by galvanostatic electrolysis at a Mo plate electrode at -50 mA cm^{-2} for 20 min in molten KF–KCl after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

(a)



(b)

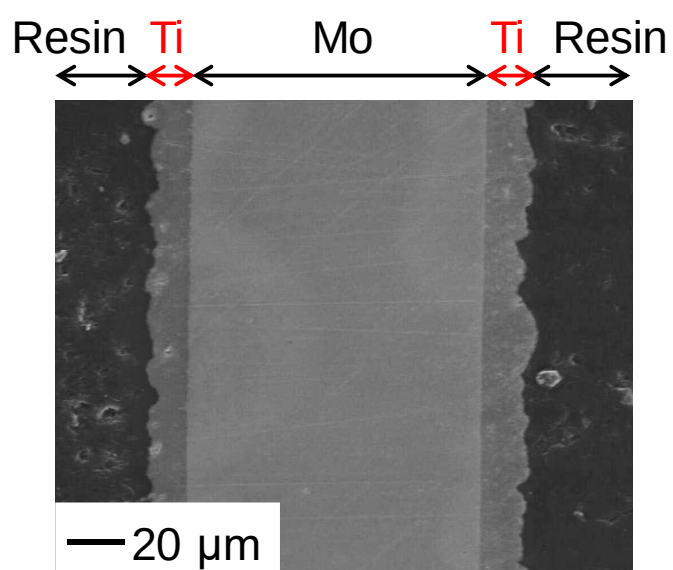


Fig. 3-4 (a) Surface and (b) cross-sectional SEM images of the sample obtained by galvanostatic electrolysis at a Mo plate electrode at -50 mA cm^{-2} for 20 min in molten KF–KCl after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

3.3.1.3 Square Wave Voltammetry

For more detailed analysis of the cathodic reaction, square wave voltammetry was conducted on the same melt. In a square wave voltammogram, the half-width of a peak, $W_{1/2}$, is given by Eq. 3-1 [1–4].

$$W_{1/2} = \frac{RT}{nF} \left\{ 3.53 + 3.46 \frac{\zeta_{SW}^2}{\zeta_{SW} + 8.1} \right\} \quad \zeta_{SW} = \frac{nFE_{SW}}{RT} \quad (3-1)$$

Here R is the universal gas constant, T is the temperature, n is the number of electrons transferred, F is the Faraday constant, f is the frequency, E_{SW} is the amplitude of the SW pulses, and ΔE is the potential increment of a staircase potential ramp. Fig. 3-5 shows the square wave voltammogram obtained at $f = 5$ Hz, $E_{SW} = 20$ mV, and $\Delta E = 2$ mV, in which the background current correction has been conducted. A fitted curve using the Gaussian function is also plotted. The voltammogram

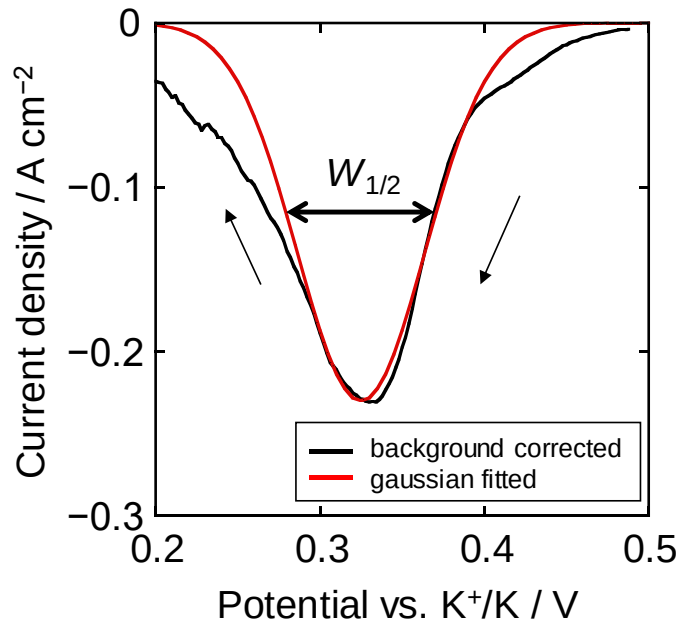


Fig. 3-5 Square wave voltammograms at a Mo flag electrode in molten KF–KCl after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K. $f = 5$ Hz, $E_{SW} = 20$ mV, and $\Delta E = 2$ mV.

exhibits a single peak with a half width of 90 mV. The peak potential is observed at 0.33 V, corresponding to the potential at which cathodic current sharply increases in the cyclic voltammogram. The background corrected voltammogram deviates from the fitted curve around 0.4 V, which may be the result of the formation of a solid solution of Ti in Mo. In the potential region more negative than 0.3 V, the voltammogram also deviates from the fitted curve, which is explained by the increase of electrode area due to nucleation and growth of Ti. The number of transferred electrons is calculated to be 3.3 from the peak half width. Thus, the cathodic current peak at 0.33 V is reasonably interpreted as the reduction of Ti(III) ions to Ti metal. This result also indicates that Ti(II) ions are not formed in KF–KCl molten salt. Chen *et al.* also reported that Ti(II) ions disappeared in NaCl–KCl–K₂TiF₆ (3 wt%) melts at 973 K when the added amounts of KF exceeded 10 wt% [5].

3.3.2 Oxidation of Ti(III) Ions

3.3.2.1 Cyclic Voltammetry

Fig. 3-6(a) shows the cyclic voltammograms obtained at a Pt flag electrode in the positive potential region. The scan rates were varied from 0.20 V s⁻¹ to 10 V s⁻¹ with 60% in-situ IR compensation. At each scan rate, a pair of redox current peaks is observed at around 1.8 V. This redox reaction is considered a reversible process because the peak potential is constant regardless of scan rate. For a reversible reaction, the following relationship holds between the anodic peak potential (E_{ap}) and the cathodic peak potential (E_{cp}) [6].

$$E_{ap} - E_{cp} \cong 2.3RT/nF \quad (3-2)$$

Since the difference of peak potential in Fig. 3-6(a) is 0.20 V, the number of transferred electrons is calculated to be 0.91 by Eq. 3-2. Thus, the redox reaction around 1.8 V corresponds to the redox reaction of Ti(III)/Ti(IV).

Further, the concentration ratio of Ti(III) to Ti(IV) ions was calculated. The equilibrium potential of Ti(III)/Ti(IV) redox reaction, E , is determined by Nernst equation (Eq. 3-3).

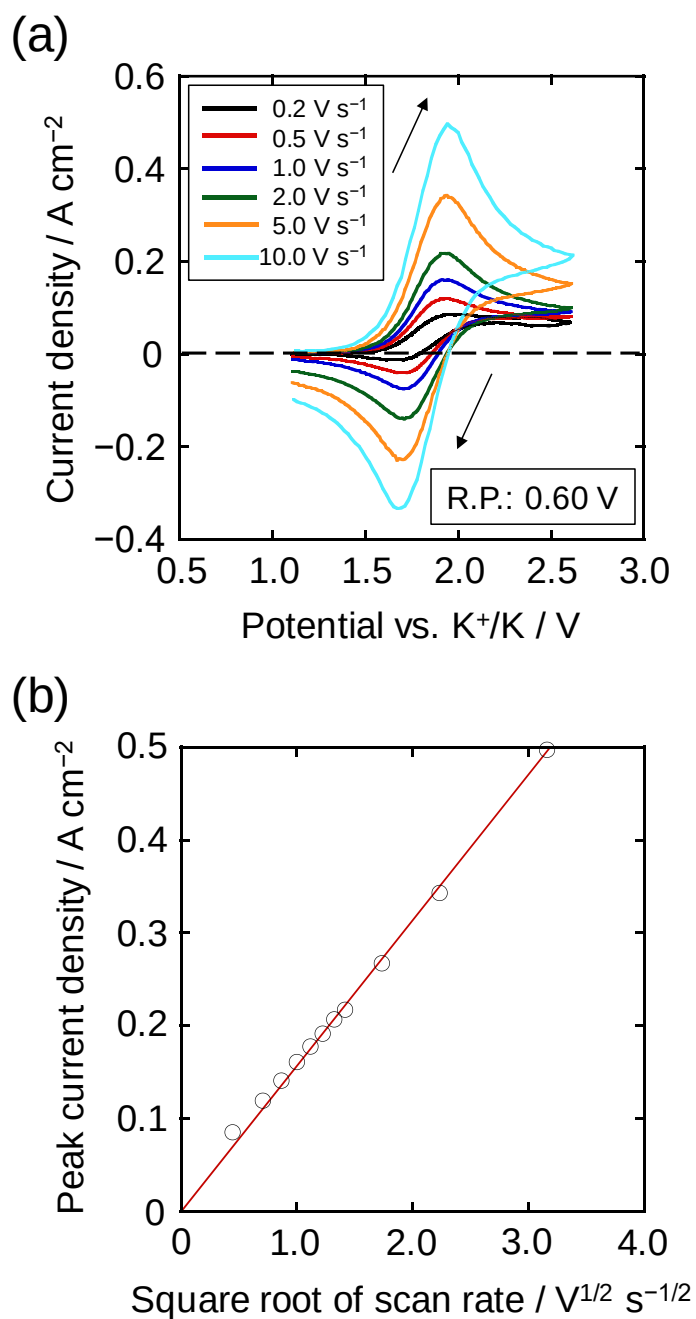


Fig. 3-6 (a) Cyclic voltammograms at a Pt flag electrode in molten KF–KCl after the addition of K₂TiF₆ (0.50 mol%) and sponge Ti (0.33 mol%) at various scan rates at 923 K. (b) Dependence of anodic peak current density on scan rate.

$$E = E^{\circ'} - \frac{RT}{F} \ln \frac{c_{\text{Ti(III)}}}{c_{\text{Ti(IV)}}} \quad (3-3)$$

Here, $E^{\circ'}$ is the standard formal redox potential, and $c_{\text{Ti(III)}}$ and $c_{\text{Ti(IV)}}$ are concentrations of Ti(III) and Ti(IV) ions, respectively. In the present experiment, E was measured to be 0.60 V from the rest potential of the Pt electrode which was considered to be determined by the equilibrium potential of Ti(III)/Ti(IV) redox reaction. The value of $E^{\circ'}$ is calculated to be 1.82 V from the averaged value of E_{ap} and E_{cp} from the cyclic voltammogram [6]. Thus, the concentration ratio of Ti(III) to Ti(IV) ions is calculated to be 4.6×10^6 , which confirms that almost all Ti(IV) ions were transformed to Ti(III) ions by the comproportionation reaction of Reaction 1-14.

3.3.2.2 Determination of Diffusion Coefficient of Ti(III) Ions by Cyclic

Voltammetry and Chronoamperometry

The diffusion coefficient of Ti(III) ions in KF–KCl molten salt was determined by the obtained cyclic voltammograms in Fig. 3-6. When a reaction is reversible and both the reactants and products are soluble, the anodic peak current (I_{ap}) is given by Eq. 3-4.

$$I_{\text{ap}} = 0.446FAc_{\text{Ti(III)}}(D_{\text{Ti(III)}}Fv/RT)^{1/2} \quad (3-4)$$

Here, A is the electrode area, $D_{\text{Ti(III)}}$ is the diffusion coefficient of Ti(III) ions, and v is the scan rate. The volume concentration of ions in the electrolyte, $c_{\text{Ti(III)}}$, is calculated using the density of the KF–KCl melt (KF:KCl = 45:55 mol%, $\rho = 1.74 \text{ g cm}^{-3}$ at 923 K) and the result of ICP-AES for the melt. The density is estimated by an extrapolation of the reported data for the KF–KCl compositions of 37:63 and 50:50 mol% in the temperature range of 1050–1250 K [7]. The concentration is calculated to be $1.75 \times 10^{-4} \text{ mol cm}^{-3}$. Fig. 3-6(b) shows the plots of anodic peak current densities against the square roots of the scan rates. From Eq. 3-4 and the slope of the plots,

the value of $D_{\text{Ti(III)}}$ is determined to be $3.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 923 K.

The diffusion coefficient of Ti(III) was also measured by chronoamperometry. When the rate determining step is the diffusion of ions, the current-time response follows the Cottrell equation [8]. The current, I , is proportional to the reciprocal of the square root of time, t .

$$I = \frac{FAD_{\text{Ti(III)}}^{1/2}c_{\text{Ti(III)}}}{\pi^{1/2}t^{1/2}} \quad (3-5)$$

The value of $D_{\text{Ti(III)}}$ can be determined from the slope of the plot of the current density versus the reciprocal of the square root of time.

For the evaluation, the potential should be set in the mass-transfer-limited region. Thus, 2.3 V and 2.4 V were selected because they were more positive than the peak potential for Ti(III) oxidation, as obtained from the cyclic voltammogram. Fig. 3-7(a) shows the chronoamperograms at a Pt flag electrode. The two chronoamperograms overlap and the anodic current densities asymptotically approach 0.10 A cm^{-2} after two seconds, indicating a diffusion-limited current. Fig. 3-7(b) shows the relationship between the current density and the reciprocal of the square root of time. Both the plots of 2.3 V and 2.4 V have a proportional relation in the range of $3 < t^{-1/2} < 6 \text{ s}^{-1/2}$. At small $t^{-1/2}$ values, the observed relationship deviates from the Cottrell equation because the growth of diffusion layer is not infinite. From the data in the range of $3 < t^{-1/2} < 6 \text{ s}^{-1/2}$, the diffusion coefficient of Ti(III) ions at 923 K is calculated to be $3.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The diffusion coefficient obtained by cyclic voltammetry is smaller than the one obtained by chronoamperometry. Although in-situ IR compensation was conducted in cyclic voltammetry, the highest compensation ratio without potential instability was 60%. Thus, the actual potential sweep rates were lower than the specified ones due to IR drops, which explains the smaller diffusion coefficient. Considering this, the value obtained by chronoamperometry, $3.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, should be more accurate. The value is 1.4-times larger than the reported value of $2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in molten LiF–NaF–KF at 973 K [9], which is likely due to the difference in the viscosities

of the molten salts.

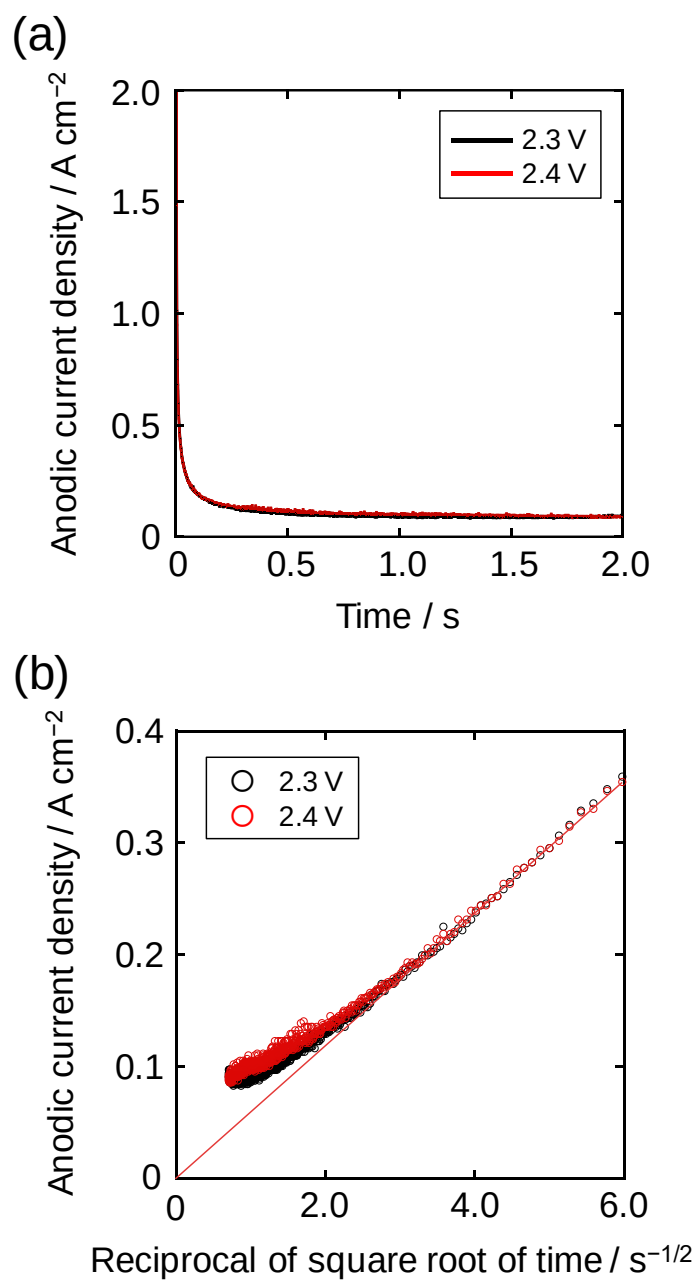


Fig. 3-7 (a) Chronoamperograms at a Pt flag electrode at 2.3 V and 2.4 V in molten KF–KCl after the addition of K_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K. (b) Relationship of the current density and the reciprocal of square root of time.

3.4 Conclusion

The electrochemical behavior of Ti(III) ions was investigated in the KF–KCl eutectic melt after the addition of 0.50 mol% of K_2TiF_6 and 0.33 mol% of sponge Ti at 923 K. The cathodic reaction around 0.33 V vs. K^+/K was determined to be the reduction of Ti(III) ions to Ti metal from the results of cyclic voltammetry, square wave voltammetry, and SEM/EDX and XRD analyses of the deposits. The anodic reaction around 1.82 V in cyclic voltammetry was found to be the electrochemically reversible oxidation of Ti(III) ions to Ti(IV) ions. The completion of the comproportionation reaction from Ti(IV) and Ti(0) to Ti(III) was confirmed by the calculation of the concentration ratio of Ti(III) to Ti(IV). The diffusion coefficient of Ti(III) ions at 923 K was determined to be $3.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ by chronoamperometry.

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Chapter 4

Optimization of Electrolysis Conditions for Ti Film Electrodeposition from Water-Soluble KF–KCl Molten Salts

4.1 Introduction

In Chapter 2, the electrodeposition of Ti films in KF–KCl molten salt has been demonstrated. However, the optimum conditions such as Ti(III) concentration and current density for obtaining adherent, compact, and smooth Ti films have not been clarified. Thus, in the present chapter, the effects of Ti(III) ion concentration and current density on the morphology of Ti electrodeposits are investigated to determine the optimum conditions. After adding various amounts of K_2TiF_6 and sponge Ti, the concentration of Ti(III) ions, i.e., the concentration of K_3TiF_6 , in the melt is calculated from the results of ICP-AES. The optimal conditions for electrodepositing adherent, compact, and smooth Ti films are evaluated via SEM observations of the deposits. Finally, the corrosion resistance of the Ti-coated Ni plate is measured in artificial seawater by linear sweep voltammetry.

4.2 Experiment

4.2.1 Electrodeposition of Ti

A preparation method of KF–KCl molten salt, an experimental apparatus and analysis methods are almost the same as Chapters 2 and 3. Some important and/or different points are

described below.

The working electrode was a Ni plate (Nilaco Corp., 10 mm × 10 mm in size, thickness: 0.1 mm, 99.95%), a Mo flag (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.95%), a Ni flag (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.98%), or a Pt flag (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.98%). Prior to the experiments, the Ni, Mo, and Pt electrodes were washed with ethanol and well dried. A Ti rod (Nilaco Corp., diameter: 3.0 mm, 99.5%) was used as the counter and reference electrodes. The electrolyzed samples on the Ni plates were soaked in distilled water at room temperature for 10 min to remove the salt adhered to the deposits. The surface and cross-section of the samples were observed by SEM (Keyence Corp., VE-8800). Prior to the observation of the cross section, the samples were cut at the center and embedded in acrylic resin. Then, the samples were polished by a cross-section polisher (CP; Hitachi, Ltd., IM4000) and coated with Au using an ion-sputtering apparatus (Hitachi, Ltd., E-1010). The Ti ion concentration in the molten salt was determined using ICP-AES (Hitachi, Ltd., SPECTRO BLUE). A small portion of molten salt was sampled and dissolved in 50 ml of HNO₃ aqueous solution (pH = 1, prepared from Tama Chemical Corp., AA-100 grade, 68 wt%).

4.2.2 Corrosion Resistance Test

A total of 50 ml of artificial seawater (BizScience Co., Ltd., Aquamarine) was used as an electrolyte to measure the corrosion resistance of the Ti-coated Ni plate. In addition to this plate, Ni (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.98%) and Ti (Nilaco Corp., 10 mm × 10 mm, thickness: 0.1 mm, 99.5%) plates were also tested for comparison. As the reference electrode, an Ag/AgCl electrode in saturated KCl aq. was used. The potential was given with reference to the potential of the standard hydrogen electrode (SHE). A Pt plate (Nilaco Corp., 10 mm × 10 mm, thickness: 0.1 mm, 99.98%) was used as the counter electrode.

4.3 Results and Discussion

4.3.1 Ti(III) Ions Concentration

Prior to electrodeposition, the concentration and electrochemical behavior of Ti(III) ions were investigated. As described in Chapters 2 and 3, almost all of the Ti ions exist as Ti(III) ions in the KF–KCl eutectic melt after the addition of K_2TiF_6 and sponge Ti. Thus, the Ti concentration determined by ICP-AES directly corresponds to the Ti(III) concentration. Since the comproportionation reaction to form Ti(III) ions (Reaction 1-14) is equivalent to Reaction 4-1, hereafter in this chapter, the K_3TiF_6 concentration is used instead of the Ti(III) ion concentration.

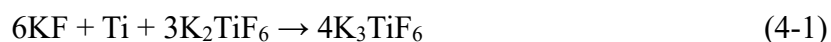


Table 4-1 shows the K_3TiF_6 concentration at various added amounts of K_2TiF_6 and sponge Ti. The theoretical value of the K_3TiF_6 concentration was calculated according to Eq. 4-1 from the added amount of K_2TiF_6 . Notably, the theoretical values in Table 4-1 are higher than the four-thirds of the added K_2TiF_6 because comproportionation reaction (Reaction 4-1) results in consumption of

Table 4-1 K_3TiF_6 concentration determined using ICP-AES in molten salt after additions of K_2TiF_6 and sponge Ti at 923 K.

Added K_2TiF_6 / mol%	Added Ti / mol%	K_3TiF_6 concentration / mol%	
		Analyzed	Theoretical
0.20	0.13	0.28	0.27
0.50	0.33	0.70	0.67
1.00	0.67	1.43	1.36
1.50	1.00	1.48	2.05

KF and decrease of the total moles of KF–KCl molten salt. When 0.20–1.00 mol% of K_2TiF_6 were added, the obtained K_3TiF_6 concentrations were nearly the same as the theoretical values. This agreement indicates almost all of the added K_2TiF_6 was converted to K_3TiF_6 according to Reaction 4-1. However, with the addition of 1.50 mol% of K_2TiF_6 , the obtained K_3TiF_6 concentration (1.48 mol%) was lower than the theoretical value (2.05 mol%). This result indicates that the solubility of K_3TiF_6 is 1.48 mol% in the KF–KCl eutectic melt at 923 K.

To further confirm the solubility, electrochemical measurement was conducted in KF–KCl after adding various amounts of K_2TiF_6 (0, 0.20, 0.50, 1.00, and 1.50 mol%) and sponge Ti (0, 0.13, 0.33, 0.67, and 1.00 mol%). Fig. 4-1(a) shows cyclic voltammograms measured at a Pt flag electrode from 1.4 V in the positive direction. At each concentration, a pair of Ti(IV)/Ti(III) redox current peaks is observed. Fig. 4-1(b) shows the anodic peak current density plotted against the added amount of K_2TiF_6 . The peak current linearly increases from blank to 1.0 mol% but negatively deviates from the linear relationship at 1.5 mol%. This behavior is explained by the Ti(III) ion solubility, i.e., the K_3TiF_6 solubility. The anodic peak current density is also plotted against the K_3TiF_6 concentration determined using ICP-AES in Fig. 4-1(b). The current linearly increases with the K_3TiF_6 concentration up to 1.48 mol%, which also confirms the K_3TiF_6 solubility to be 1.48 mol%.

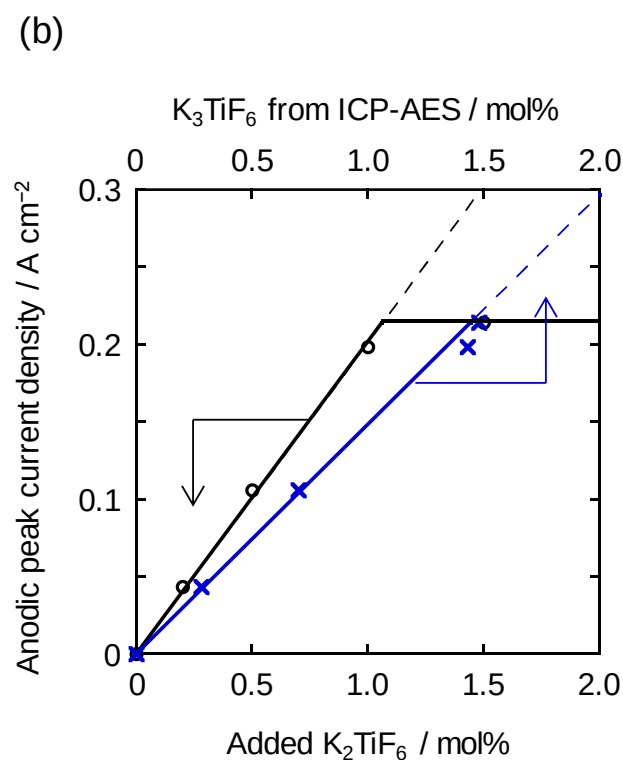
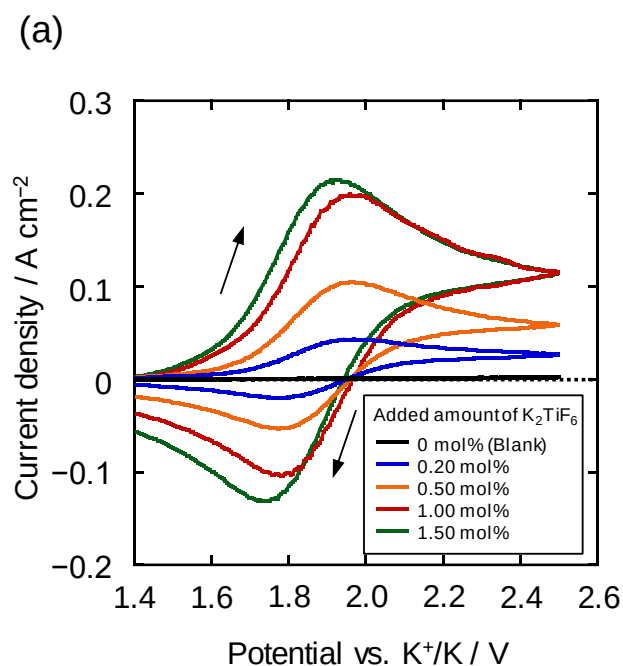


Fig. 4-1 (a) Cyclic voltammograms at a Pt flag electrode in molten KF–KCl after adding various amounts of K₂TiF₆ (0, 0.20, 0.50, 1.00, and 1.50 mol%) and sponge Ti (0, 0.13, 0.33, 0.67, and 1.00 mol%) at 923 K. Scan rate: 0.50 V s⁻¹. (b) Dependence of anodic peak current density on the added amount of K₂TiF₆. The X-axis on the top denotes the K₃TiF₆ concentration determined using ICP-AES.

4.3.2 Morphology of Electrodeposited Ti

Galvanostatic electrolysis was conducted using a Ni plate electrode at various current densities from 25 to 150 mA cm⁻² in KF–KCl–K₃TiF₆ (0.28, 0.70, and 1.43 mol%). Here, the reduction current was expressed as a positive value. The electric charge density was fixed at 60 C cm⁻² for all electrolysis. The theoretical thickness of the electrodeposited Ti is 22 μm. Fig. 4-2 shows a comparison of the potential transient curves during electrolysis at 25–100 mA cm⁻² in KF–KCl–K₃TiF₆ (0.70 mol%). The potential was more negative than 0.4 V vs. K⁺/K from which the reduction current of Ti(III) to Ti metal was observed. The potential is more negative at higher current density. Particularly, the potential becomes more negative than 0.25 V during the beginning at 100 mA cm⁻². At such a negative potential, K metal fog possibly occurs in the molten KF–KCl [1]. At 100 mA cm⁻², an increase in electrode area is also suggested because a positive shift in the potential was observed during the electrolysis.

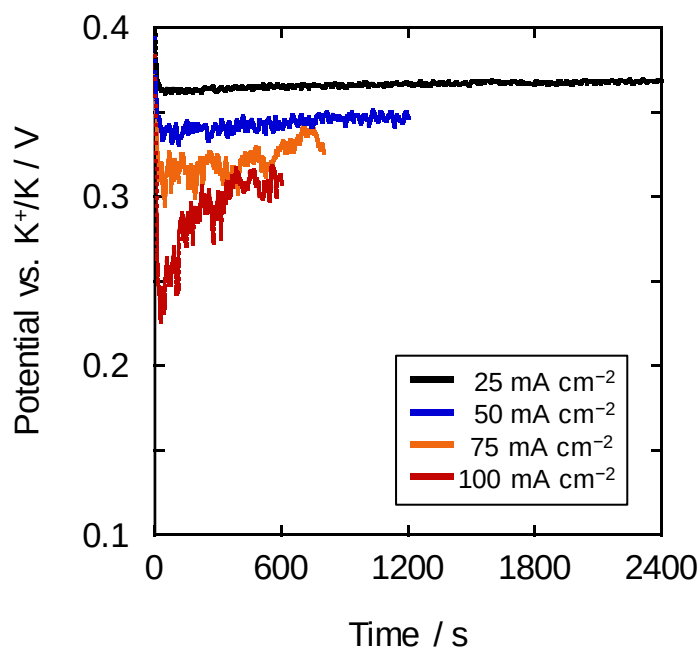


Fig. 4-2 Potential transient curves during galvanostatic electrolysis at Ni electrodes at various current densities in molten KF–KCl–K₃TiF₆ (0.70 mol%) at 923 K.

Fig. 4-3 shows the optical images of the obtained samples after washing with distilled water at room temperature for 10 min. At the highest current density for each K_3TiF_6 concentration, the obtained deposits were peeled from the Ni substrate during water washing because of poor adhesion. At low current densities of 0.70 and 1.43 mol% K_3TiF_6 , silver-colored deposits were obtained.

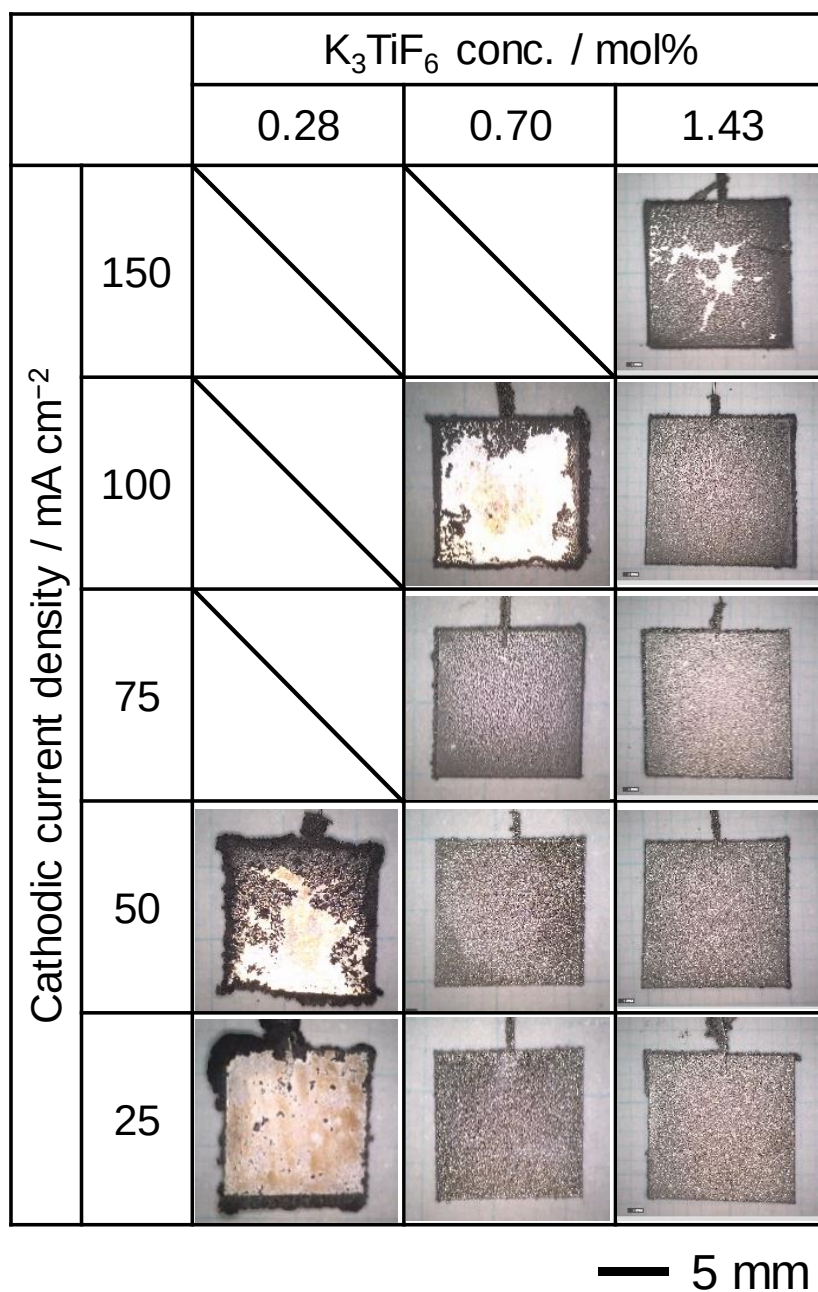


Fig. 4-3 Optical images of the samples obtained by galvanostatic electrolysis at Ni plates in molten $\text{KF-KCl-K}_3\text{TiF}_6$ at 923 K. Charge density: 60 C cm^{-2} .

Fig. 4-4(a) shows the XRD pattern of the deposit obtained at 50 mA cm^{-2} at 0.70 mol% K_3TiF_6 . No peaks other than metallic Ti and Ni substrate are observed, which suggests that the solidified salt was removed by water washing. To further confirm the salt removal, EDX analysis was conducted for the deposit as shown in Fig. 4-4(b). Only Ti is detected and all the constituent elements of molten salt electrolyte (K, F, and Cl) are below the detection limits, which confirms complete removal of the solidified salts. At a lower concentration of 0.28 mol% K_3TiF_6 , the appearance including the surface color is different from that of the other samples even at 25 mA cm^{-2} . Powder-like Ti was deposited at the edge parts, which is explained by the high local-current density at the edges. As the result, the Ti film on most parts of the substrate is as thin as a few micrometers, which is confirmed by cross-sectional SEM observation shown in Fig 4-5.

Fig. 4-6 and Fig. 4-7 show the surface and cross-sectional SEM images of the samples obtained in molten $\text{KF-KCl-K}_3\text{TiF}_6$ (0.70 and 1.43 mol%) at various current densities, respectively. Adherent, compact, and smooth Ti films are obtained at $25\text{--}50 \text{ mA cm}^{-2}$ for 0.70 mol% K_3TiF_6 and at $25\text{--}75 \text{ mA cm}^{-2}$ for 1.43 mol% K_3TiF_6 . Under other conditions of higher current densities, coral-like or uneven Ti deposits are obtained. As a typical good Ti film, Fig. 4-8 shows the (a) surface and (b) cross-sectional SEM images of 50 mA cm^{-2} and 0.70 mol% K_3TiF_6 . The thickness of the films on the center part of the substrate is $10\text{--}15 \text{ }\mu\text{m}$. Current efficiency calculated from the weight increase is as high as 90%. Despite the high current efficiency, the thickness of the Ti film at the center part is thinner than the theoretical value of $22 \text{ }\mu\text{m}$. This difference is possibly caused by current concentration on the electrode edges.

At higher current densities, for example, at 75 mA cm^{-2} for 0.70 mol% K_3TiF_6 , coral-like growth perpendicular to the substrate is observed, as shown in Fig. 4-9(a). In some cases, nodule Ti is found at the surface of the Ti films, as shown in Fig. 4-9(b). The nodular and coral-like morphologies are because of the preferential deposition at convex parts of the Ti deposits.

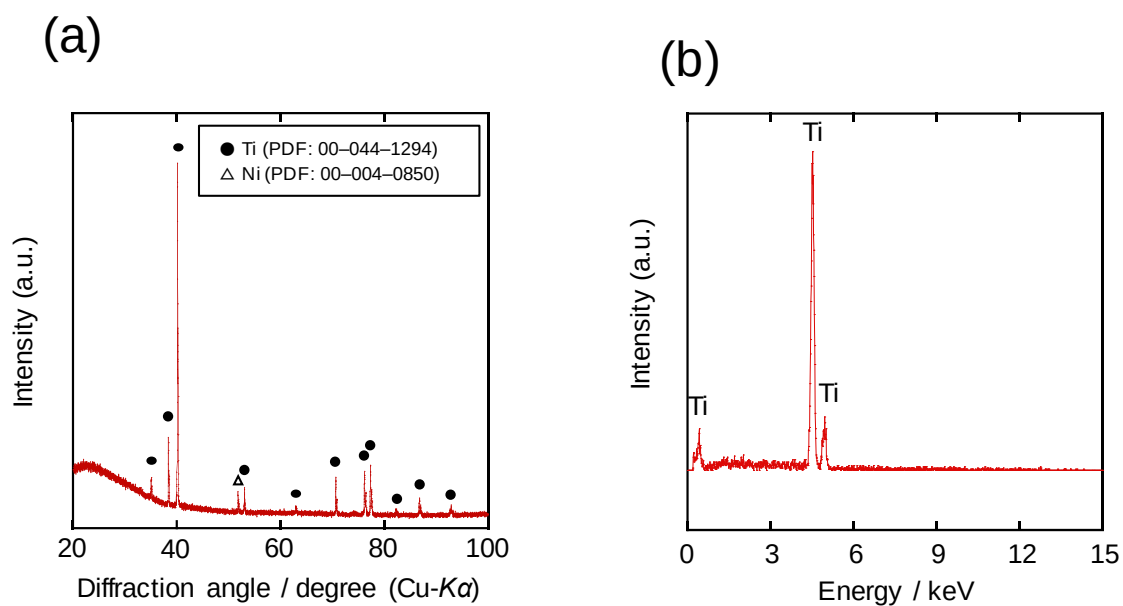


Fig. 4-4 (a) An XRD pattern and (b) an EDX spectrum of the surface of the sample obtained by galvanostatic electrolysis at 25 mA cm^{-2} at a Ni plate in $\text{KF-KCl-K}_3\text{TiF}_6$ (0.70 mol%) at 923 K. Charge density: 60 C cm^{-2} .

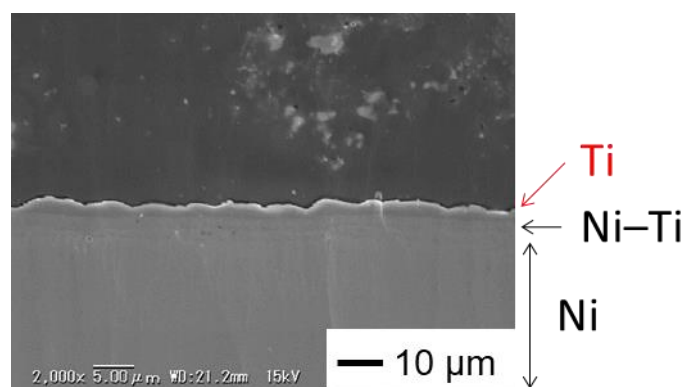


Fig. 4-5 A cross-sectional SEM image of the sample obtained by galvanostatic electrolysis at 25 mA cm^{-2} at a Ni plate in $\text{KF-KCl-K}_3\text{TiF}_6$ (0.29 mol%) at 923 K. Charge density: 60 C cm^{-2} .

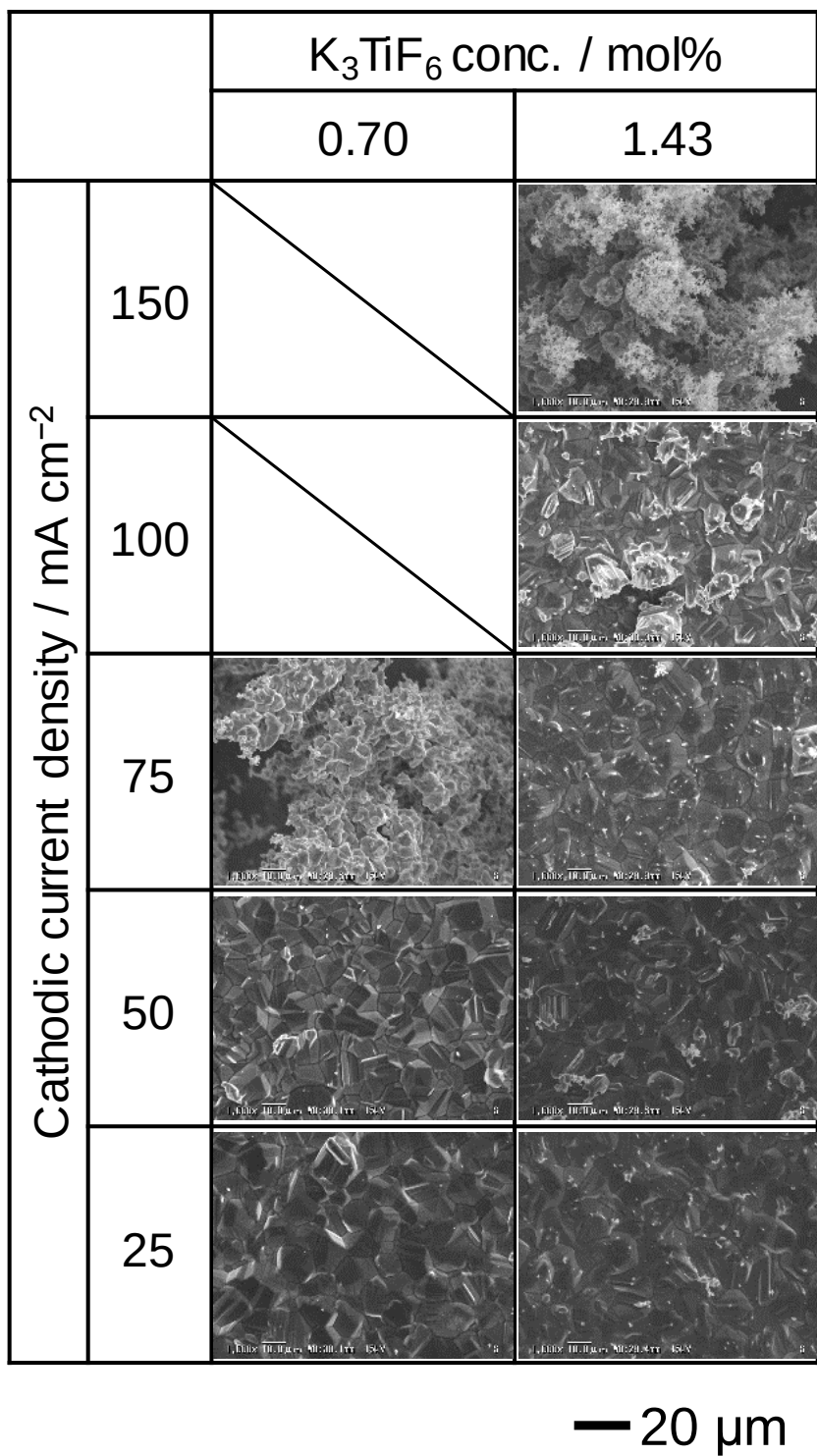


Fig. 4-6 Surface SEM images of the samples obtained by galvanostatic electrolysis at Ni plates in KF–KCl–K₃TiF₆ at 923 K. Charge density: 60 C cm⁻².

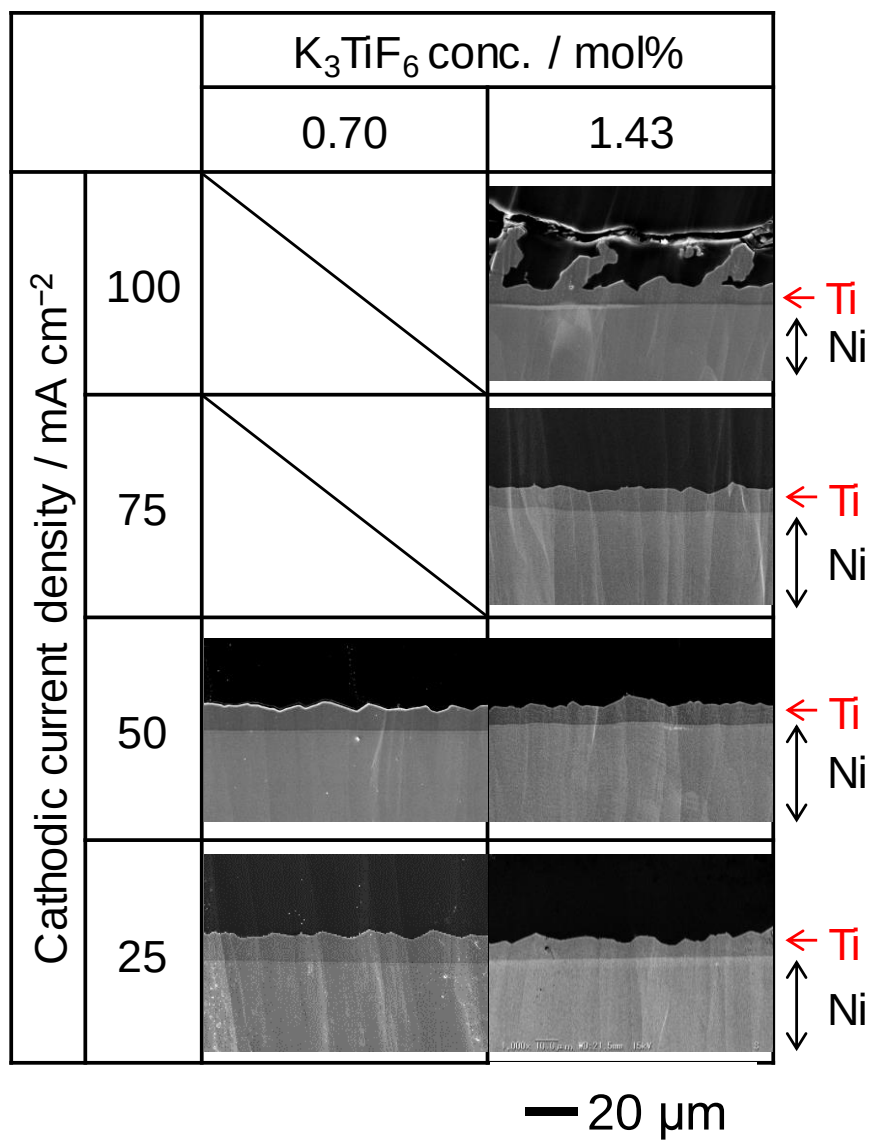
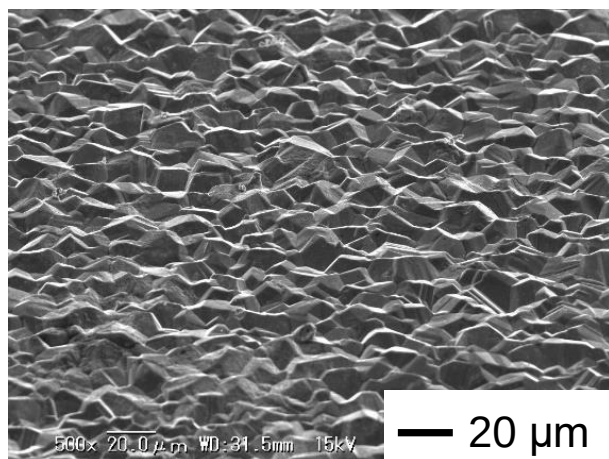


Fig. 4-7 Cross-sectional SEM images of the samples obtained by galvanostatic electrolysis at Ni plates in KF–KCl–K₃TiF₆ at 923 K. Charge density: 60 C cm⁻².

(a)



(b)

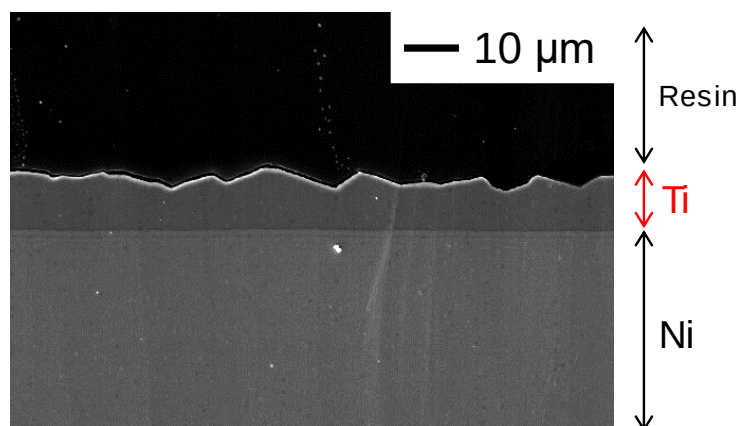
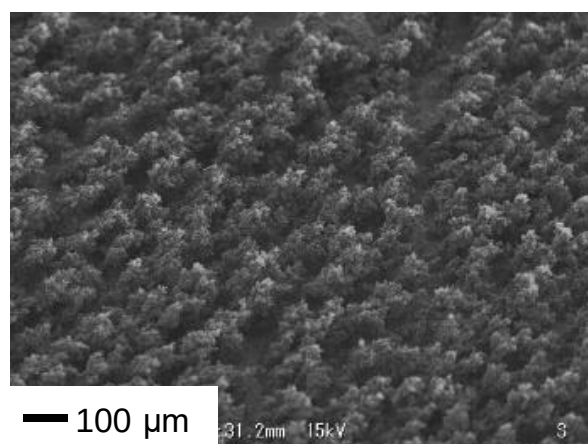


Fig. 4-8 (a) Surface and (b) cross-sectional SEM images of the sample obtained by galvanostatic electrolysis at 50 mA cm^{-2} at a Ni plate in $\text{KF-KCl-K}_3\text{TiF}_6$ (0.70 mol%) at 923 K. Charge density: 60 C cm^{-2} .

(a)



(b)

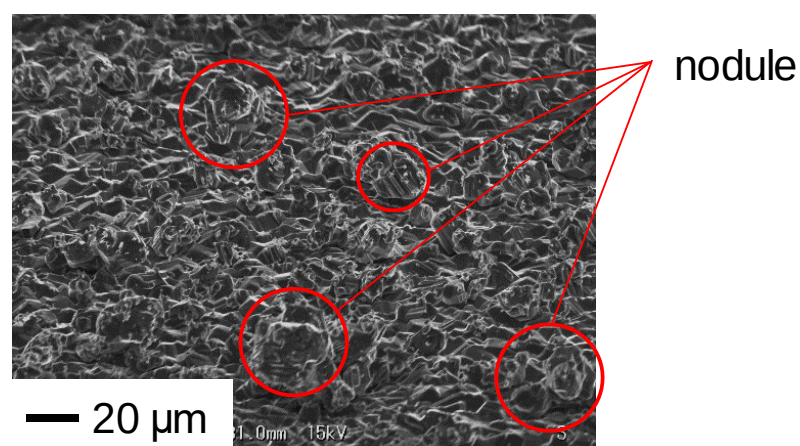


Fig. 4-9 Surface SEM images of the samples obtained by galvanostatic electrolysis at Ni plates at (a) 75 mA cm^{-2} in $\text{KF-KCl-K}_3\text{TiF}_6$ (0.70 mol%) and (b) 100 mA cm^{-2} in $\text{KF-KCl-K}_3\text{TiF}_6$ (1.43 mol%) at 923 K. Charge density: 60 C cm^{-2} .

In the previous literature, Robin *et al.* reported that compact and well-crystallized Ti films were obtained from LiF–NaF–KF–K₃TiF₆ at 34.5–50 mA cm⁻² at 873 and 973 K [2]. The conditions for obtaining good Ti films in LiF–NaF–KF–K₃TiF₆ are similar to those of the present study. Furthermore, the morphology of the obtained Ti films is nearly the same for both the LiF–NaF–KF and the KF–KCl systems. Thus, Ti films having a similar quality as the molten LiF–NaF–KF system can be obtained from the water-soluble KF–KCl molten salt.

4.3.3 Corrosion Resistance Test

To evaluate the corrosion resistance of the Ti-coated Ni plate, linear sweep voltammetry was conducted in artificial seawater at 295 K. The Ti-coated Ni plate was prepared by galvanostatic electrolysis at 25 mA cm⁻² for 40 min in KF–KCl–K₃TiF₆ (1.43 mol%). The estimated thicknesses of the Ti films are 10–15 μm. Fig. 4-10 shows the obtained voltammograms in which the potential

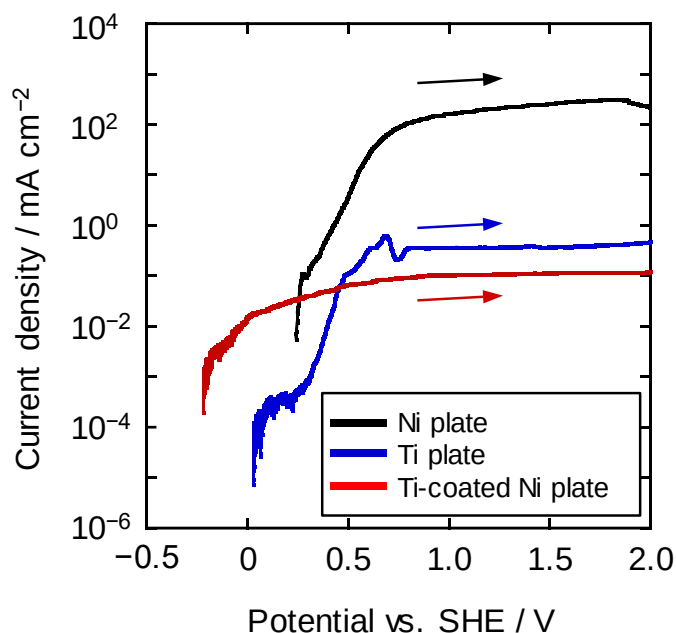


Fig. 4-10 A linear sweep voltammogram of Ti-coated Ni in artificial seawater at 295 K. Scan rate: 1 mV s⁻¹. The Ti-coated Ni plate was prepared by galvanostatic electrolysis at 25 mA cm⁻² for 40 min in molten KF–KCl–K₃TiF₆ (1.43 mol%). Linear sweep voltammograms of the Ni and Ti plates are shown for comparison.

was swept from the open-circuit potential to 2.0 V vs. SHE at a scan rate of 1 mV s⁻¹. For comparison, the voltammograms at the Ni and Ti plates are also shown. At the Ni plate electrode, the anodic current resulting from Ni dissolution rapidly increases from the open-circuit potential. However, for the Ti-coated sample, the anodic current is kept under a limit of 0.1 mA cm⁻² until 2.0 V. This behavior is similar to that of the Ti plate. Such excellent corrosion resistance is a result of the formation of passivation oxide films [3,4]. The results demonstrate that the electrodeposited Ti films completely coated the Ni substrate without any voids. The different open-circuit potential and the obtained currents between the Ti plate and Ti-coated sample possibly relate to the amount of impure elements.

4.4 Conclusion

The conditions for the electrodeposition were optimized in terms of adherent, compact, and smooth Ti films in KF–KCl–K₃TiF₆ at 923 K is investigated. The solubility of K₃TiF₆ was confirmed to be 1.48 mol% using ICP-AES. Galvanostatic electrolysis was conducted on Ni plate substrates at various K₃TiF₆ concentrations (0.28, 0.70, and 1.43 mol%) and current densities (25–150 mA cm⁻²). Surface and cross-sectional SEM observations showed that adherent, compact, and smooth Ti films were obtained at 25–50 mA cm⁻² for 0.70 mol% K₃TiF₆ and at 25–75 mA cm⁻² for 1.43 mol% K₃TiF₆. Finally, linear sweep voltammetry at a Ti-coated Ni plate electrode showed high corrosion resistance in artificial seawater at 295 K, proving that no cracks or voids exist in the Ti films.

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Chapter 5

Electrochemical Behavior of Ti(III) Ions in LiF–LiCl Molten Salt: Comparison with the Behavior in KF–KCl Molten Salt

5.1 Introduction

In the previous chapters, compact and relatively smooth Ti films have been obtained from the KF–KCl eutectic melt (KF:KCl = 45:55 mol%, 923 K) containing Ti(III) ions. The redox potentials of Ti(III)/Ti(0) and Ti(IV)/Ti(III) couples have been determined to be 0.33 V vs. K^+/K (peak potential of SWV) and 1.82 V (standard formal redox potential), respectively. In the present chapter, electrochemical behavior of Ti(III) ions in LiF–LiCl (LiF:LiCl = 45:55 mol%, 923 K) is investigated by cyclic voltammetry and square wave voltammetry. In a similar manner to the KF–KCl, Ti(III) ions are prepared by adding 0.50 mol% of Li_2TiF_6 and 0.33 mol% of sponge Ti. The effect of cations in fluoride–chloride melt on the electrochemical behavior of Ti(III) ions is discussed by comparing the results of LiF–LiCl and KF–KCl.

5.2 Experimental

Reagent-grade LiF (Kojundo Chemical Laboratory Co., Ltd., >99%) and LiCl (Kojundo Chemical Laboratory Co., Ltd., >99%) were dried under vacuum at 453 K for more than 72 h and at 773 K for 24 h. The salts were mixed in the prescribed composition (molar ratio of LiF:LiCl = 45:55, 300 g) and the mixture was loaded in a Ni crucible (Chiyoda Industry Manufacturing Plant

Co., Ltd., outer diameter: 98 mm, inner diameter: 96 mm, height: 102 mm). The crucible was placed at the bottom of a stainless-steel vessel in an air-tight Kanthal container. The electrochemical measurements were conducted in a dry Ar atmosphere at 923 K in a glove box. After the blank measurements in molten LiF–LiCl, 0.50 mol% of Li₂TiF₆ and 0.33 mol% of sponge Ti (Kojundo Chemical Laboratory Co., Ltd., >99%) were added to the melt. Here, 0.33 mol% of sponge Ti corresponds to approximately twice the amount necessary to generate Ti(III) ions from 0.50 mol% of Li₂TiF₆, according to Eq. 1-14. Prior to the experiment, powdery Li₂TiF₆ was prepared from aqueous H₂TiF₆ solution (Morita Chemical Industry Co., Ltd., 40%) and Li₂CO₃ (FUJIFILM Wako Pure Chemical Co., Ltd., >99.0%) according to the method reported by Janz *et al.* [1]. First, 37 g of Li₂CO₃ were added to 200 mL of aqueous H₂TiF₆ solution, and then ultrapure water was added to give a final volume of 300 mL.



The Li₂TiF₆ product was completely soluble; therefore, any precipitate that formed was removed by filtration because it could contain impurities like TiO₂. Solid Li₂TiF₆ was recovered by evaporation of the solution under reduced pressure. The thus-obtained Li₂TiF₆ was dried under vacuum at 453 K for more than 6 h and pulverized in a mortar under dry Ar atmosphere in a glove box.

Electrochemical measurements and galvanostatic electrolysis were conducted by a three-electrode method using an electrochemical measurement system (Hokuto Denko Corp., HZ-7000). The working electrodes were Mo plate (Nilaco Corp., 10 mm × 10 mm, thickness: 0.1 mm, 99.95%), Mo flag (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.95%), Au flag (Nilaco Corp., diameter: 3.0 mm, thickness: 0.1 mm, 99.98%), and glassy carbon rod (Tokai Carbon Co., Ltd., diameter: 3.0 mm) electrodes. Ti rods (Nilaco Corp., diameter: 3.0 mm, 99.5%) were used as the counter and reference electrodes. In the blank measurement, a Pt wire (Nilaco Corp., diameter: 1.0

mm, 99.98%) was used as the quasi-reference electrode. The potential of the reference electrodes was calibrated with reference to a dynamic Li^+/Li potential, determined by cyclic voltammetry on a Mo electrode. When necessary, the potential was expressed based on Cl_2/Cl^- and F_2/F^- potentials, calculated from the theoretical decomposition voltage of the salt. The calibration method is explained in the next section. The melt temperature was measured using a type-K thermocouple. The salt adhering to the deposits was removed by ultrasonic washing in distilled water for 10 min.

The surface and cross-section of the sample were observed by using scanning electron microscopy (SEM; Thermo Fisher Scientific Inc., Phenom Pro Generation 5). Before the observation of the cross section, the samples were embedded in an acrylic resin and polished with emery papers and buffing compounds. The samples were then coated with Au using an ion sputtering apparatus (Hitachi, Ltd., E-101) to impart conductivity. The deposits were also characterized by energy-dispersive X-ray (EDX; AMETEK Co. Ltd., EDAX Genesis APEX2) and X-ray diffraction (XRD; Rigaku Corp., Ultima IV, $\text{Cu-K}\alpha$ line) analyses. A small portion of the molten salt was sampled by the suction method using a borosilicate glass tube (Pyrex[®], outer diameter: 6 mm, inner diameter: 4 mm) and dissolved in aqueous HNO_3 solution ($\text{pH} = 1$, prepared from Tama Chemical Corp., AA-100 grade, 68 wt%). The solution was analyzed by using inductive coupled plasma atomic emission spectroscopy (ICP-AES; Hitachi, Ltd., SPECTRO BLUE) to determine the Ti ion concentration in the sampled molten salt.

5.3 Results and Discussion

5.3.1 Electrochemical Window of LiF-LiCl Molten Salt

Prior to the measurement of Ti(III) ions in LiF-LiCl , the electrochemical window of the used molten LiF-LiCl at 923 K was determined. Fig. 5-1(a) shows the cyclic voltammogram in a negative potential region at a Mo flag electrode. The cathodic current due to the formation of Li metal fog increases gradually from 0.2 V vs. Li^+/Li . Then, the current increases rapidly from 0 V, corresponds to the deposition of liquid Li metal.

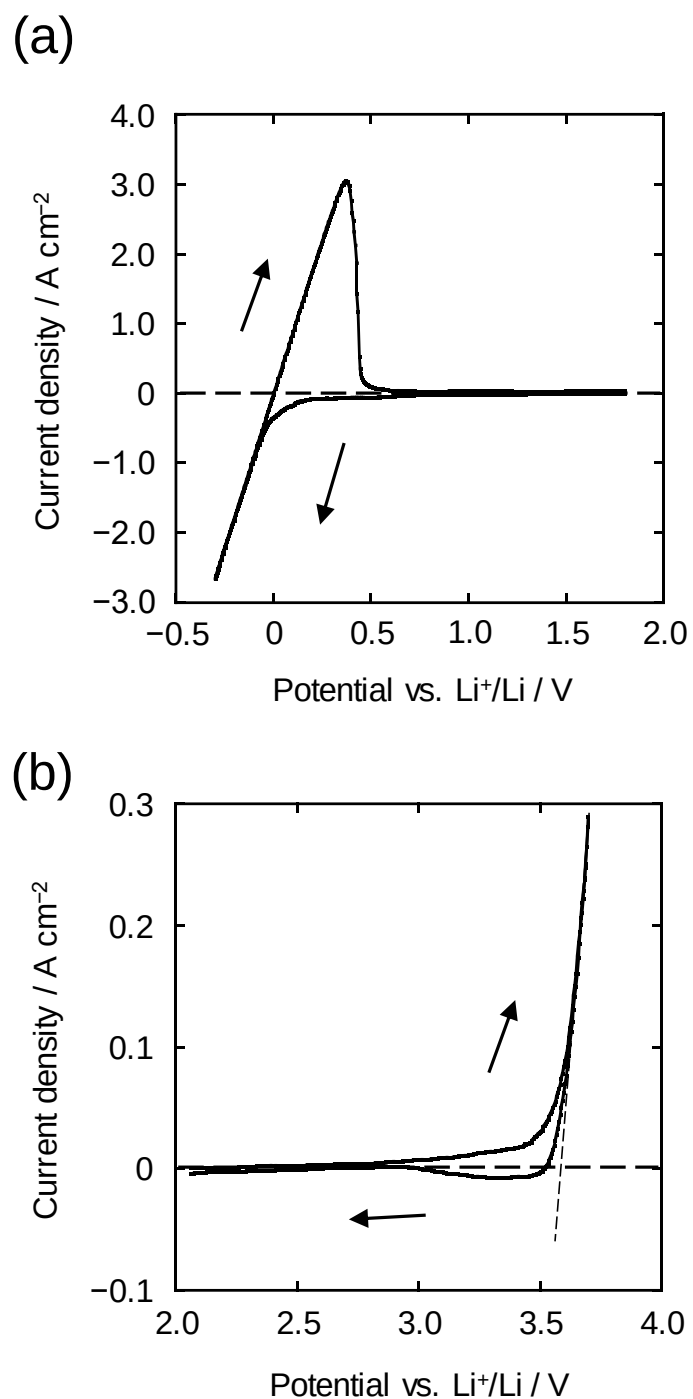


Fig. 5-1 Cyclic voltammograms (a) in the negative potential region at a Mo flag electrode and (b) in the positive potential region at a glass-like carbon rod electrode in molten LiF–LiCl at 923 K. Scan rate: 0.5 V s^{-1} .



After reversal of the scan direction, anodic current due to Li metal dissolution is observed. The potential at zero current in the linear variation region during the positive sweep can be considered the redox potential of Li^+/Li . Fig. 5-1(b) shows the cyclic voltammogram in a positive potential region at a glass-like carbon electrode. A sharp increase in anodic current due to Cl_2 gas evolution is observed around 3.5 V.



Based on this result, the electrochemical window of LiF–LiCl molten salt (LiF:LiCl = 45:55 mol%, 923 K) is determined to be 3.5 V. This value is in good agreement with the theoretical electrochemical window of LiF–LiCl, 3.51 V, which has been calculated from the standard Gibbs energy of formation of $\text{LiCl}(l)$, $-333.81 \text{ kJ mol}^{-1}$ [2], assuming the activity of LiCl to be 0.55.

5.3.2 Reduction of Ti(III) Ions

The electrochemical reduction of Ti(III) ions was investigated using cyclic voltammetry and square wave voltammetry. Fig. 5-2(a) shows the cyclic voltammogram in a negative potential region obtained at a Mo flag electrode in molten LiF–LiCl after the addition of 0.50 mol% of Li_2TiF_6 and 0.33 mol% of sponge Ti at 923 K. Cathodic current increases from approximately 1.30 V vs. Li^+/Li and forms a peak at 1.18 V. After reversal of the scanning direction at 1.00 V, the corresponding anodic current peak is observed at 1.31 V. For more detailed analysis of the cathodic reaction, square wave voltammetry was conducted on the same melt. The square wave voltammogram obtained at $f = 5 \text{ Hz}$, $E_{\text{SW}} = 20 \text{ mV}$, and $\Delta E = 10 \text{ mV}$ (Fig. 5-2(b)) shows a single peak at 1.19 V vs. Li^+/Li . Here, f is the frequency, E_{SW} is the amplitude of the SW pulses, and ΔE

is the potential increment of a staircase potential ramp. In a square wave voltammogram, the half-width of a peak, $W_{1/2}$, is given by Eq. 5-4 [3–6].

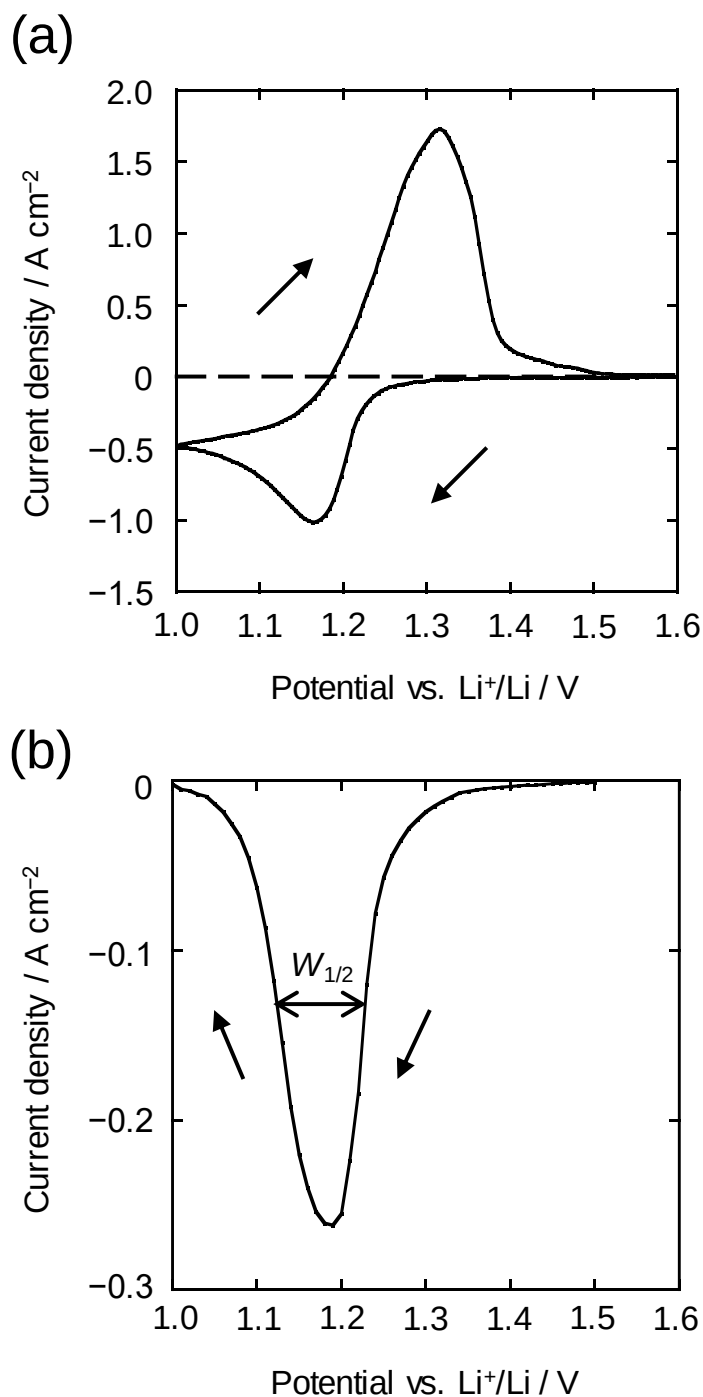


Fig. 5-2 (a) A Cyclic voltammogram and (b) a square wave voltammogram at a Mo flag electrode in molten LiF–LiCl after the addition of Li_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K. $f = 5$ Hz, $E_{\text{SW}} = 20$ mV, and $\Delta E = 10$ mV.

$$W_{1/2} = \frac{RT}{nF} \left\{ 3.53 + 3.46 \frac{\zeta_{SW}^2}{\zeta_{SW} + 8.1} \right\} \quad \zeta_{SW} = \frac{nFE_{SW}}{RT} \quad (5-4)$$

Here R is the universal gas constant, T is the temperature, n is the number of electrons transferred, and F is the Faraday constant. The value of n is calculated to be 3.0 from the peak half-width of 100 mV in Fig. 5-2(b). Since the calculated value is 3.0, the reduction observed in the voltammograms in Fig. 5-2(b) is suggested to be the deposition of Ti metal.



To confirm this, galvanostatic electrolysis was conducted using a Mo plate electrode at a current density of -50 mA cm^{-2} for 20 min. Fig. 5-3 shows the potential transient curve during galvanostatic electrolysis. The potential during electrolysis was around 1.2 V vs. Li^+/Li , indicating the progress of the cathodic reaction observed in the cyclic voltammogram. As shown in the right-

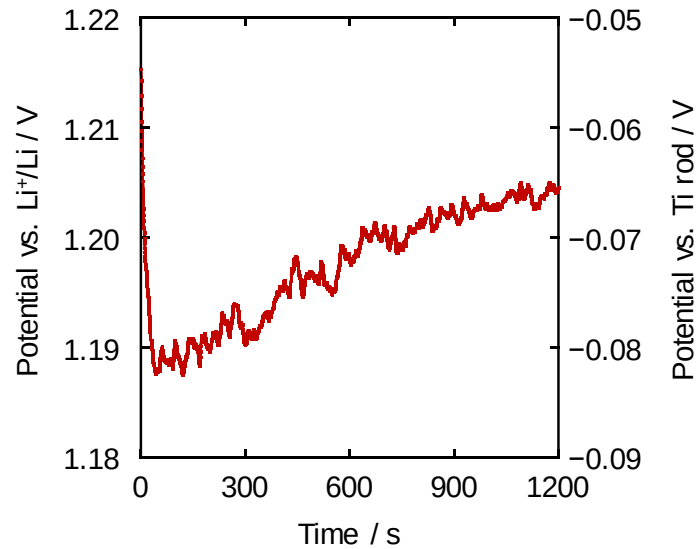
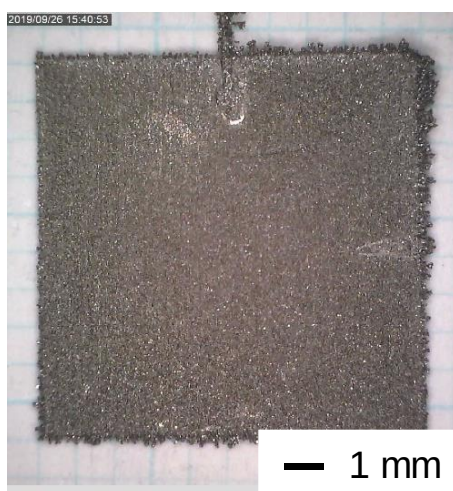


Fig. 5-3 A Potential transient curve during the galvanostatic electrolysis of a Mo plate electrode at -50 mA cm^{-2} for 20 min in LiF-LiCl after the addition of Li_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

hand potential axis, the potential was approximately -70 mV against a Ti reference electrode, which suggests the presence of concentration and activation overpotentials. The optical image of the sample after water washing (Fig. 5-4(a)) shows deposits having metallic luster covering the entire substrate. The XRD pattern of the sample (Fig. 5-4(b)) shows peaks only for metallic Ti and Ni substrate. Although LiF has low solubility in water (0.13 g per 100 g- H_2O at 293 K [7]), any

(a)



(b)

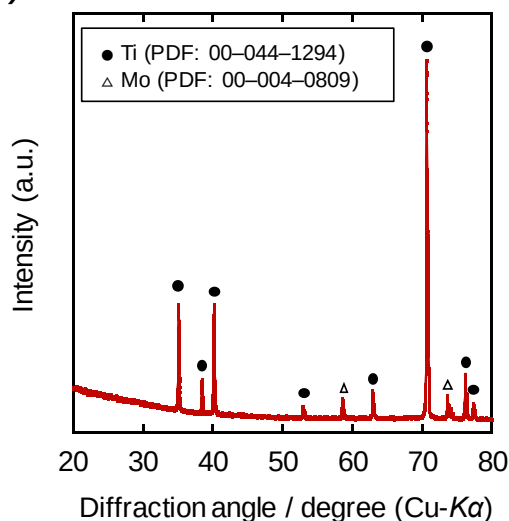


Fig. 5-4 (a) An optical image and (b) an XRD pattern of the sample obtained by galvanostatic electrolysis of a Mo plate electrode at -50 mA cm^{-2} for 20 min in molten LiF–LiCl after the addition of Li_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

adhered salts were successfully removed from the sample, likely because the dissolution of LiCl assisted the physical removal of LiF from the sample surface. The surface and cross-sectional SEM images of the sample are shown in Fig. 5-5(a) and (b), respectively. The deposits have compact grains with diameters of approximately 10 μm . Only Ti was detected by EDX analysis of the sample surface. The cross-sectional SEM image demonstrates that adherent, compact, and comparably smooth films with a thickness of around 15 μm were electrodeposited on the Mo substrate. Based

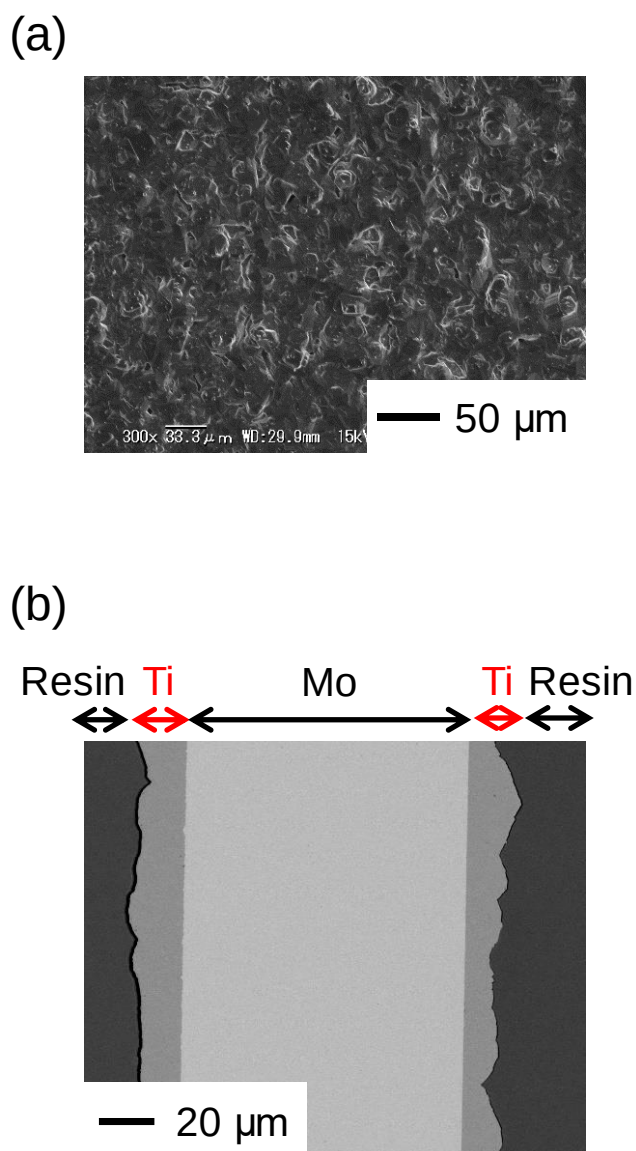


Fig. 5-5 (a) Surface and (b) cross-sectional SEM images of the sample obtained by galvanostatic electrolysis of a Mo plate electrode at -50 mA cm^{-2} for 20 min in molten LiF–LiCl after the addition of Li_2TiF_6 (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K.

on these results, the cathodic wave in the cyclic voltammogram is assigned to the reduction of Ti(III) ions to metallic Ti (Reaction 5-5).

5.3.3 Oxidation of Ti(III) Ions

The anodic oxidation of Ti(III) ions was investigated using cyclic voltammetry. Fig. 5-6(a) shows the cyclic voltammograms obtained at a Au flag electrode in a positive potential region. Scan rates were varied from 0.5 V s⁻¹ to 10.0 V s⁻¹. Pairs of redox currents are observed around 2.8 V vs. Li⁺/Li. This redox reaction is reversible process because the peak potential was constant and independent of scan rate. For a reversible reaction, the following relationship holds between the anodic peak potential (E_{ap}) and the cathodic peak potential (E_{cp}) [8],

$$E_{ap} - E_{cp} \cong 2.3RT / nF \quad (5-6)$$

Since the difference of peak potentials in Fig. 5-6(a) is 0.16 V, n is calculated to be 1.1. Thus, the observed redox currents correspond to the redox reaction of Ti(IV)/Ti(III).



Here, the standard formal redox potential, $E^{\circ'}$, is calculated as 2.78 V from the average value of the cathodic and anodic peak potentials.

The diffusion coefficient of Ti(III) ions, $D_{\text{Ti(III)}}$, in LiF–LiCl molten salt was determined from the cyclic voltammetry results. In a reversible electrochemical reaction for the soluble reactants and products, the anodic peak current (I_{ap}) is given by Eq. 5-8 [8].

$$I_{ap} = 0.446FAc_{\text{Ti(III)}}(D_{\text{Ti(III)}}Fv/RT)^{1/2} \quad (5-8)$$

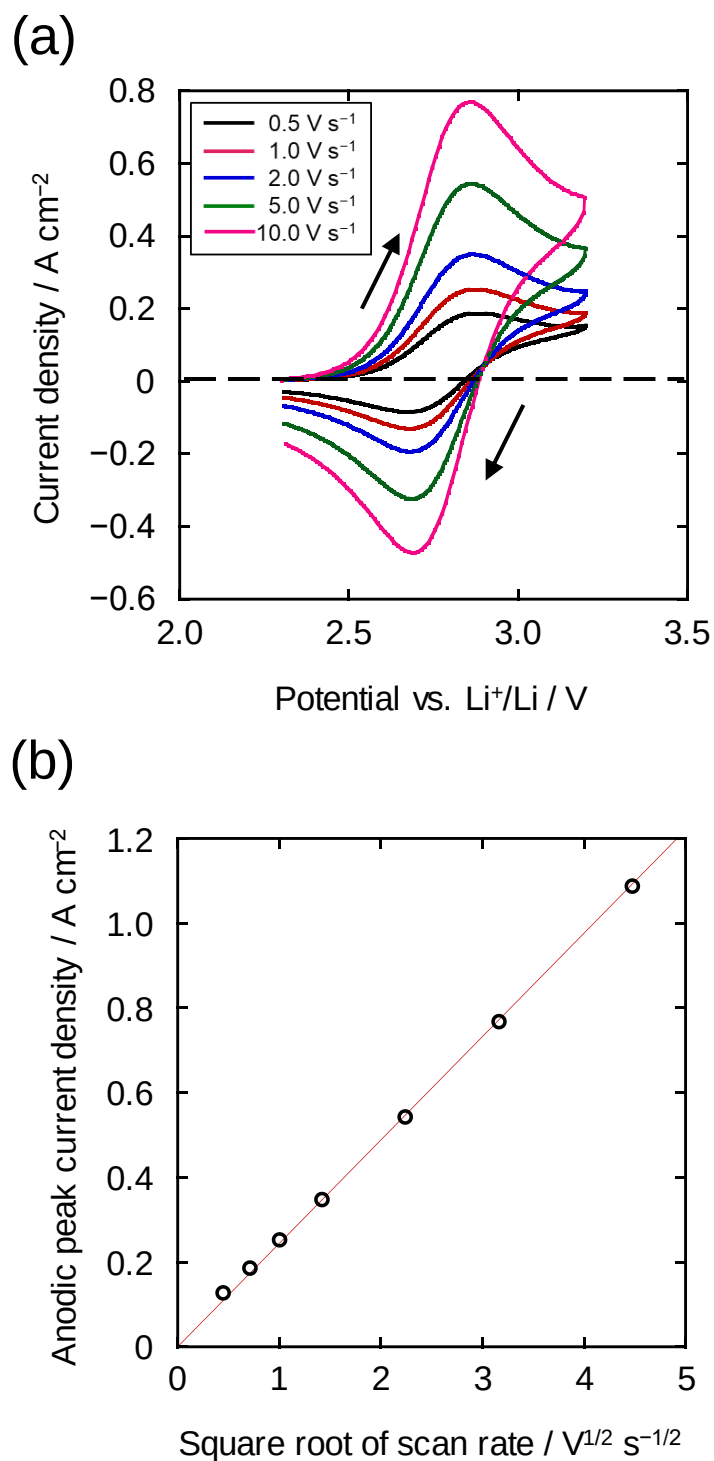


Fig. 5-6 (a) Cyclic voltammograms at a Au flag electrode in molten LiF–LiCl after the addition of Li₂TiF₆ (0.50 mol%) and sponge Ti (0.33 mol%) at various scan rates at 923 K. (b) Dependence of anodic peak current density on scan rate.

Here A is the electrode area, and ν is the scan rate. The volume concentration of ions in the electrolyte, $c_{\text{Ti(III)}}$, is calculated to be $2.88 \times 10^{-4} \text{ mol cm}^{-3}$ from ICP-AES result for the melt and its density. In this case, the density of the melt with a composition of LiF:LiCl = 45:55 mol% is estimated to be 1.58 g cm^{-3} at 923 K by extrapolating the reported data for the melts of compositions LiF:LiCl = 37:63 and 50:50 mol% in the temperature range 940–1260 K [9]. Fig. 5-6(b) shows the plots of I_{ap} vs. $\nu^{1/2}$ in the range of 0.2–20.0 V s⁻¹. The value of $D_{\text{Ti(III)}}$ is determined from the slope of the plots to be $3.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 923 K.

5.3.4 Comparison of Electrochemical Behavior of Ti(III) Ions

Table 5-1 compares the redox potentials of Ti(IV)/Ti(III) and Ti(III)/Ti(0) couples in LiF–LiCl and KF–KCl at 923 K. The potentials are expressed against the Cl₂/Cl⁻ potential, in which the conversion of potential has been conducted using the theoretical electrochemical windows of the molten salts. The theoretical electrochemical window of LiF–LiCl is 3.51 V, as calculated in section 5. 3. 1, while that of KF–KCl is calculated to be 3.63 V based on the standard Gibbs energy of KCl(*l*) at 923 K [2]. The potential of Ti(IV)/Ti(III) couple in LiF–LiCl is 1.08 V more positive than that in KF–KCl. In the case of Ti(III)/Ti(0) couple, the value in LiF–LiCl is 0.98 V more positive

Table 5-1 The redox potentials of Ti(IV)/Ti(III) and Ti(III)/Ti(0) couples in LiF–LiCl and KF–KCl.

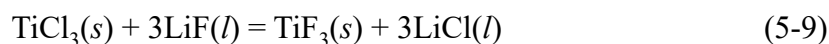
Molten salt	$E \text{ vs. Cl}_2/\text{Cl}^- / \text{V}$		$E \text{ vs. F}_2/\text{F}^- / \text{V}$		T / K	Ref.
	Ti(IV)/Ti(III)	Ti(III)/Ti(0)	Ti(IV)/Ti(III)	Ti(III)/Ti(0)		
LiF–LiCl (45:55)	-0.73*	-2.32 [†]	-2.70*	-4.29 [†]	923	Present chapter
KF–KCl (45:55)	-1.81*	-3.30 [†]	-3.11*	-4.60 [†]	923	Chapter 3

* The value of standard formal potential determined by CV.

[†] The peak potential in SWV.

that in KF–KCl. In other words, the stable potential range of Ti(III) ions in LiF–LiCl is shifted in positive direction by *ca.* 1 V compared with the KF–KCl system.

To explain the shift in potential, we first must consider the stability of the titanium complex ions from the viewpoint of thermodynamics. Since hexacoordinated titanium ions exist in molten salts [10–13], the possible titanium complex ions present in the fluoride–chloride molten salt mixture are $\text{TiF}_{6-x}\text{Cl}_x^{3-}$. To evaluate whether F^- or Cl^- anions coordinate more readily, the standard Gibbs energies for conversion from TiCl_3 to TiF_3 by the reaction with LiF or KF have been calculated based on the reported thermochemical data [2].



$$\Delta G_C^\circ = -126.01 \text{ kJ mol}^{-1} \text{ at } 923 \text{ K}$$



$$\Delta G_C^\circ = -320.67 \text{ kJ mol}^{-1} \text{ at } 923 \text{ K}$$

Since the Gibbs energies of conversion have large negative values for both the systems, the most probable form of titanium complex ions is TiF_6^{3-} . When the ligands of the titanium complex ions are only F^- , its stability should be discussed based on the potential with reference to that of the F_2/F^- couple. Thus, the redox potentials of the Ti(IV)/Ti(III) and Ti(III)/Ti(0) couples in LiF–LiCl and KF–KCl against the F_2/F^- potential are also listed in Table 1. The potential conversions have been conducted in the same manner as the conversion for the Cl_2/Cl^- potential. Although the difference in potential between LiF–LiCl and KF–KCl has decreased, there remain large differences of 0.41 V and 0.31 V for the Ti(IV)/Ti(III) and Ti(III)/Ti(0) couples, respectively.

Similar tendencies of the shifts in potential, i.e., more positive for smaller alkaline cation, were reported for pure chloride molten salts [10,11]. Table 5-2 compares the potentials of the Ti(IV)/Ti(III), Ti(III)/Ti(II), Ti(III)/Ti(0), and Ti(II)/Ti(0) couples in LiCl, LiCl–KCl, NaCl–CsCl, and CsCl molten salts at 1023 K, as reported by Song *et al.* [11]. They explained that the potential

shifts were due to the polarization power of alkaline cations, which was strongly related to cation radius. That is, smaller cations such as Li^+ have higher polarization power and strong ionic attraction to Cl^- , which results in less stable Ti chlorocomplexes. The present shifts in potential in fluoride–chloride molten salts are well explained in the same manner: the smaller cations that interact strongly with F^- reduce the stability of the Ti fluorocomplexes. Notably, the difference in potential in fluoride–chloride melts is larger than that in pure chloride melts. For example, the difference in potential for the Ti(IV)/Ti(III) couple was 0.41 V based on F_2/F^- potential between LiF–LiCl and KF–KCl, and 0.32 V based on Cl_2/Cl^- potential between LiCl and CsCl. The larger difference in fluoride–chloride melts is explained by the larger difference in interaction between $\text{Li}^+ - \text{F}^-$ and $\text{K}^+ - \text{F}^-$ than that between $\text{Li}^+ - \text{Cl}^-$ and $\text{K}^+ - \text{Cl}^-$.

Table 5-2 The redox potentials of Ti(IV)/Ti(III), Ti(III)/Ti(II), Ti(III)/Ti(0), and Ti(II)/Ti(0) couples in LiCl, LiCl–KCl, NaCl–CsCl, and CsCl molten salts [11].

Molten salt	<i>E</i> vs. Cl_2/Cl^- / V				<i>T</i> / K
	Ti(IV)/Ti(III)	Ti(III)/Ti(II)	Ti(II)/Ti(0)	Ti(III)/Ti(0)	
LiCl	–0.30*	–1.67 [†]	–1.98 [†]	—	1023
LiCl–KCl (59:41)	–0.43*	–1.70 [†]	–2.01 [†]	—	1023
NaCl–CsCl (35:65)	–0.53*	–1.88 [†]	–2.12 [†]	—	1023
CsCl	–0.62*	—	—	–1.98 [†]	1023

* The value of standard formal potential determined by CV.

[†] The half wave potential estimated from peak potential in SWV.

5.4 Conclusion

The electrochemical behavior of Ti(III) ions was investigated in LiF–LiCl melt after the addition of 0.50 mol% of Li_2TiF_6 and 0.33 mol% of sponge Ti at 923 K. The cathodic reaction at around 1.2 V vs. Li^+/Li was determined to be the reduction of Ti(III) ions to Ti metal, based on the results of cyclic voltammetry, square wave voltammetry, and XRD analyses of the deposits. The oxidation reaction of Ti(III) ions to Ti(IV) ions was reversible, with the formal standard potential of 2.78 V. The diffusion coefficient of Ti(III) ions was determined to be $3.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The potentials for Ti(III)/Ti(0) and Ti(VI)/Ti(III), with reference to the F_2/F^- potential in LiF–LiCl, were more positive than those in KF–KCl by 0.31 V and 0.41 V, respectively. Such potential differences were explained by the interactions of $\text{Li}^+ - \text{F}^-$ and $\text{K}^+ - \text{F}^-$; smaller cations interact more strongly with F^- , resulting in reduced stability of Ti fluorocomplexes.

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Chapter 6

Effect of Temperature on Ti Electrodeposition in Eutectic LiF–LiCl Molten Salt

6.1 Introduction

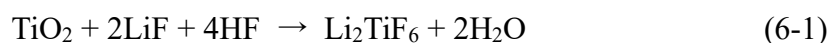
In Chapter 5, the electrodeposition of Ti films has been demonstrated in LiF–LiCl molten salt (LiF:LiCl = 45:55 mol%) at 923 K. In the present chapter, the effects of temperature on the electrochemical behavior of Ti(III) ions and the Ti electrodeposition are investigated in eutectic LiF–LiCl molten salt (LiF:LiCl = 30:70 mol%, m.p. = 774 K) in the temperature range of 823–973 K. The electrochemical behavior of Ti(III) ions is studied by cyclic voltammetry and square wave voltammetry. The activation energy for the diffusion of Ti(III) is determined by an Arrhenius plot of diffusion coefficient of Ti(III) ions. The Ti films electrodeposited at 823–973 K are analyzed by SEM to confirm the effect of temperature on the electrodeposition.

6.2 Experiment

A preparation method of LiF–LiCl molten salt, an experimental apparatus and analysis methods are almost the same as Chapter 5. Important and/or different points are described below.

After the LiF (Kojundo Chemical Laboratory Co., Ltd., >99% or FUJIFILM Wako Pure Chemical Co., Ltd., >98.0%) and LiCl (Kojundo Chemical Laboratory Co., Ltd., >99% or FUJIFILM Wako Pure Chemical Co., Ltd., >98.0%) were dried, the salts were mixed to the eutectic composition (LiF:LiCl = 30:70 mol%, 300 g). Powdery Li_2TiF_6 was prepared by the same method

as in Chapter 5 or another method according to the previous report by Tikhomirova *et al.* as follows [1]. The aqueous solution containing Li_2TiF_6 was prepared by adding 30 g of TiO_2 (anatase, FUJIFILM Wako Pure Chemical Co., Ltd., >98.5%) and 19.5 g of LiF (FUJIFILM Wako Pure Chemical Co., Ltd., >98.0%) to 150 mL of aqueous HF solution (FUJIFILM Wako Pure Chemical Co., Ltd., 46–48%).



After stirring for 1 h, the precipitates were filtered out and the obtained solution was dried in the same manner in Chapter 5. Ti(III) ions were prepared by adding Li_2TiF_6 and sponge Ti (FUJIFILM Wako Pure Chemical Co., Ltd., >99%) to the melt.

The surface and cross-section of the deposition samples were observed by scanning electron microscopy (SEM; Thermo Fisher Scientific Inc., Phenom Pro Generation 5 or Keyence Corp., VE-8800). The surface roughness (S_a) was also analyzed by SEM (Thermo Fisher Scientific Inc., Phenom Pro Generation 5).

6.3 Results and Discussion

6.3.1 Electrochemical Measurement

The electrochemical reduction of Ti(III) ions was investigated by cyclic voltammetry and square wave voltammetry. Fig. 6-1 shows (a) the cyclic voltammogram and (b) the square wave voltammogram in the negative potential region obtained at a Mo flag electrode in molten LiF–LiCl after the addition of 0.50 mol% of Li_2TiF_6 and 0.33 mol% of sponge Ti at 923 K. Cathodic current is observed from 1.4 V vs. Li^+/Li in the both voltammograms. The peak potential of square wave voltammogram is 1.21 V. As described in Chapters 3 and 5, in a square wave voltammogram, the half width of a peak, $W_{1/2}$, is given by Eq. 6-2 [2–5].

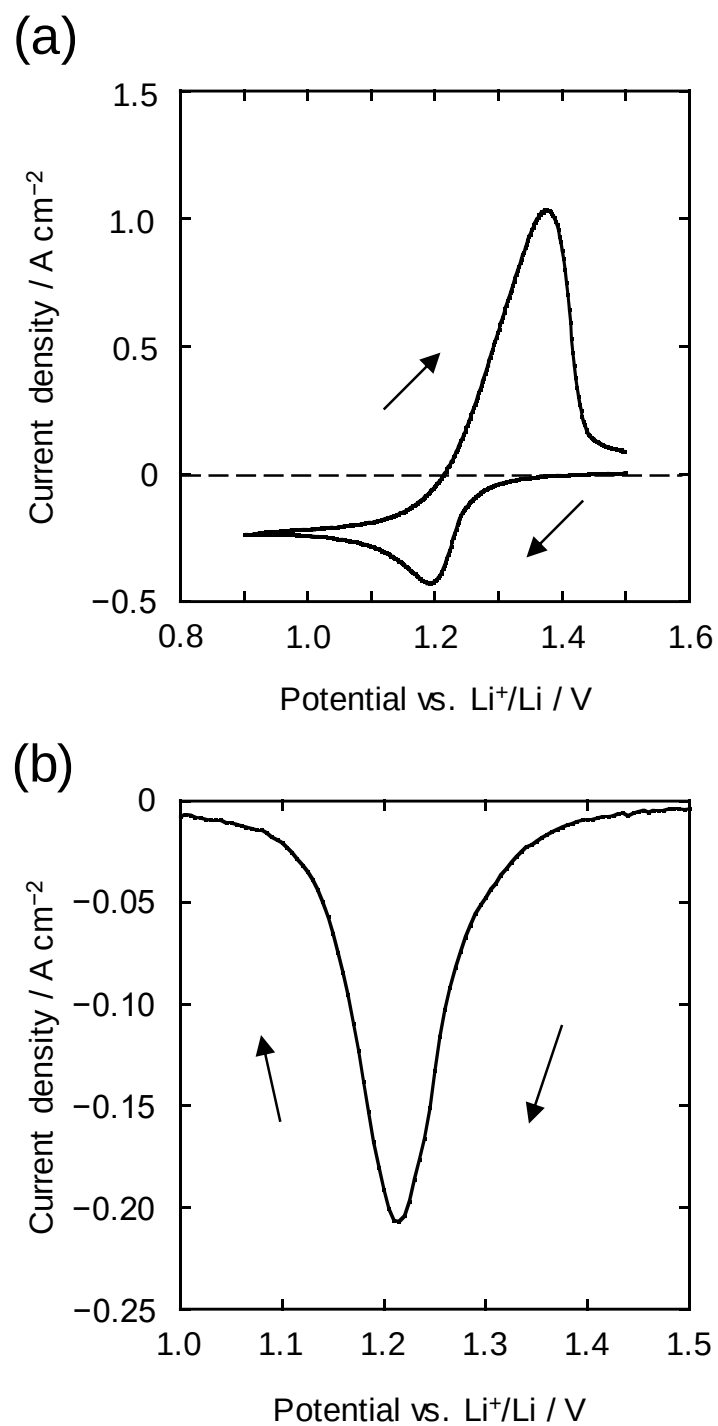


Fig. 6-1 (a) A cyclic voltammogram and (b) a square wave voltammogram at a Mo flag electrode in molten LiF–LiCl after the addition of Li₂TiF₆ (0.50 mol%) and sponge Ti (0.33 mol%) at 923 K. (a) Scan rate: 0.2 V s⁻¹. (b) $f = 5$ Hz, $E_{\text{SW}} = 20$ mV, and $\Delta E = 10$ mV.

$$W_{1/2} = \frac{RT}{nF} \left\{ 3.53 + 3.46 \frac{\zeta_{SW}^2}{\zeta_{SW} + 8.1} \right\} \quad \zeta_{SW} = \frac{nFE_{SW}}{RT} \quad (6-2)$$

Here R is the universal gas constant, T is the temperature, n is the number of electrons transferred, F is the Faraday constant, f is the frequency, E_{SW} is the amplitude of the SW pulses, and ΔE is the potential increment of a staircase potential ramp. The number of transferred electrons calculated by the half width of 90 mV is 3.3. This value suggests that the reduction observed in the voltammograms in Fig. 6-1 is the deposition of Ti metal from Ti(III) ions.



The electrochemical oxidation of Ti(III) ions was further investigated by cyclic voltammetry. Fig. 6-2(a) shows the cyclic voltammograms obtained at a Au flag electrode in the positive potential region at 923 K. The scan rates were varied from 0.5 V s⁻¹ to 10.0 V s⁻¹. Pairs of redox currents are observed around 2.8 V vs. Li⁺/Li. Because of the constant potential at various scan rates, the redox reaction is a reversible process. For a reversible reaction, the following equation holds between the anodic peak potential (E_{ap}) and the cathodic peak potential (E_{cp}) [6].

$$E_{ap} - E_{cp} \cong 2.3RT/nF \quad (6-4)$$

The number of transferred electrons calculated by the peak difference of 0.19 V is 0.96. Therefore, the redox reaction observed in Fig. 6-2(a) corresponds to the redox reaction of Ti(IV)/Ti(III).



Moreover, the standard formal redox potential, $E^{\circ'}$, is calculated as 2.83 V from the average value

of the cathodic and anodic peak potentials. At other temperatures, the reactions of Ti(III)/Ti(0) and Ti(IV)/Ti(III) were also observed around 1.2 V and 2.8 V, respectively.

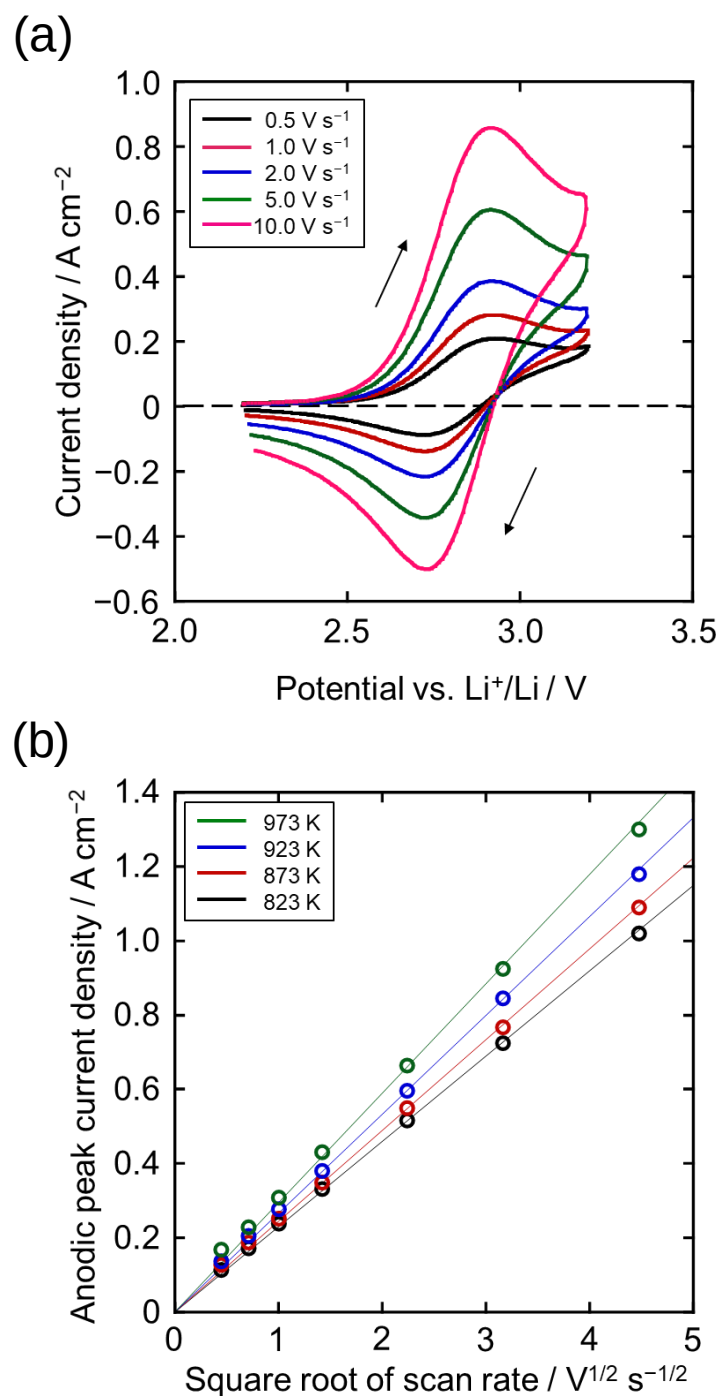


Fig. 6-2 (a) Cyclic voltammograms at a Au flag electrode in molten LiF–LiCl after the addition of Li₂TiF₆ (0.50 mol%) and sponge Ti (0.33 mol%) at various scan rates at 923 K. (b) Dependence of anodic peak current density on scan rate at 823, 873, 923, and 973 K.

The diffusion coefficient of Ti(III) ions in LiF–LiCl molten salt was determined by the cyclic voltammograms. In a reversible electrochemical reaction for soluble reactants and products, the anodic peak current (I_{ap}) is given by Eq. 6-6.

$$I_{ap} = 0.446FAc_{\text{Ti(III)}}(D_{\text{Ti(III)}}Fv/RT)^{1/2} \quad (6-6)$$

Here, A is the electrode area, $D_{\text{Ti(III)}}$ is the diffusion coefficient of Ti(III) ions, and v is the scan rate. The volume concentration of Ti(III) ions in the electrolyte, $c_{\text{Ti(III)}}$, is calculated from the ICP-AES results for the melt and the density of the LiF–LiCl melt. The density of the melt with a composition of LiF:LiCl = 30:70 mol% is estimated by an extrapolation of the reported data for the melts of LiF:LiCl = 37:63 and 25:75 mol% in the temperature range of 940–1260 K [7]. The estimated values are 1.58, 1.56, 1.54, and 1.52 g cm⁻³ at 823, 873, 923, and 973 K, respectively. Fig. 6-2(b) shows the plots of anodic peak current density against square root of the scan rate in the range of 0.2 V–20.0 V at 823, 873, 923, and 973 K. The values of $D_{\text{Ti(III)}}$ at 823, 873, 923, and 973 K are determined from the slope of the plots to be 3.3, 4.1, 5.2, and 7.0×10^{-5} cm² s⁻¹, respectively.

Fig. 6-3 shows the Arrhenius plots created from temperature dependence of $D_{\text{Ti(III)}}$. When the diffusion is dominated by an Arrhenius-type behavior, the diffusion coefficient varies according to Eq. 6-7.

$$D_{\text{Ti(III)}} = D'_{\text{Ti(III)}} \exp(-W/RT) \quad (6-7)$$

Here, $D'_{\text{Ti(III)}}$ is constant and W is the activation energy for diffusion. From the slope in Fig. 6-3, the activation energy is calculated to be 33.3 kJ mol⁻¹, and $D_{\text{Ti(III)}}$ is expressed as a function of temperature.

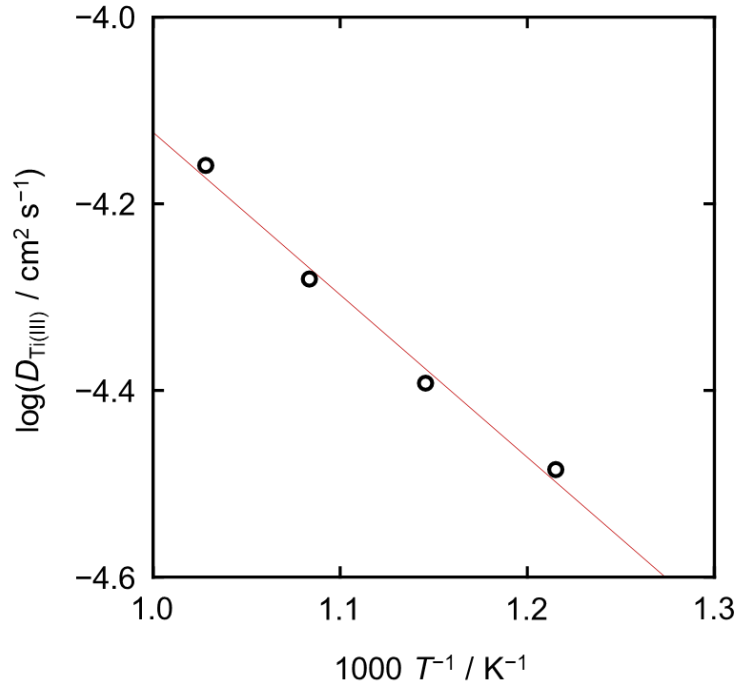


Fig. 6-3 Arrhenius plots of diffusion coefficient of Ti(III) ions in molten LiF–LiCl after the addition of Li₂TiF₆ (0.50 mol%) and sponge Ti (0.33 mol%) at 823, 873, 923, and 973 K.

$$D_{Ti(III)} = 4.17 \times 10^{-3} \times 10^{-1.74 \times 10^3/T} \quad (6-8)$$

Generally, the relationship between the diffusion coefficient and viscosity, μ , is known as the Stokes-Einstein equation,

$$\mu D = kT / 6\pi\alpha \quad (6-9)$$

where k is the Boltzmann constant, and α is the radius. From Eqs. 6-6 and 6-8, the following equation is obtained.

$$\ln(\mu / T) = \ln(k / 6D_{Ti(III)}\alpha) + W / RT \quad (6-10)$$

From the reported temperature dependence of viscosity for both a single LiF melt and a single LiCl melt [7], the calculated activation energies for LiF and LiCl are 26.0 and 29.3 kJ mol⁻¹, respectively. These activation energies are approximately the same as the values for the diffusion of Ti(III) ions. This result indicates that the diffusion of Ti(III) ions is related to the viscosity of molten salts according to the Stokes-Einstein equation.

6.3.2 Electrodeposition of Ti

To investigate an effect of temperature on morphology of Ti electrodeposits, galvanostatic electrolysis was conducted at the various temperatures. Fig. 6-4 shows the optical and surface SEM

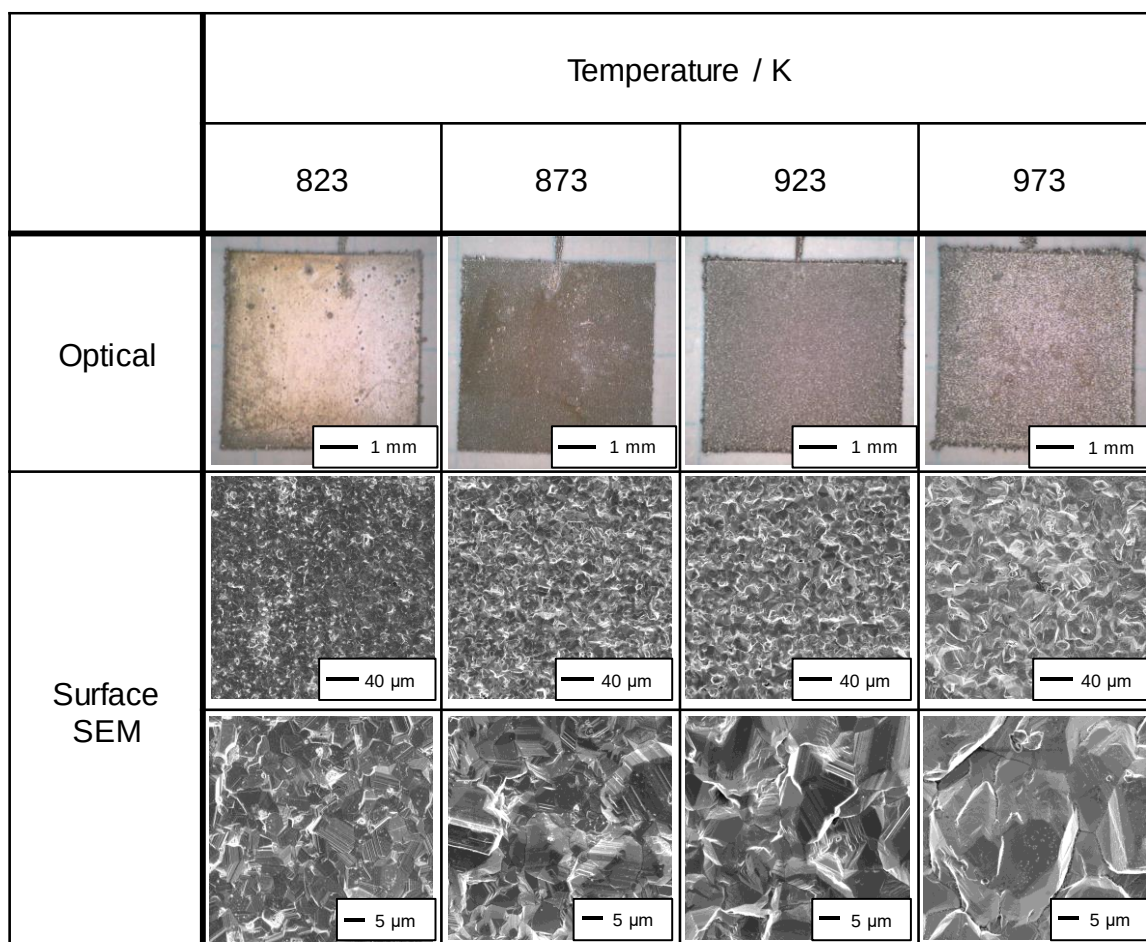


Fig. 6-4 Optical and surface SEM images of the samples obtained by galvanostatic electrolysis of Ni plates in molten LiF–LiCl after the addition of Li₂TiF₆ (2.00 mol%) and sponge Ti (1.33 mol%) at 823, 873, 923, and 973 K. Cathodic current density and time: 100 mA cm⁻² for 10 min.

images of the samples obtained by galvanostatic electrolysis of Ni plates in molten LiF–LiCl after the addition of Li_2TiF_6 (2.00 mol%) and sponge Ti (1.33 mol%) at 823, 873, 923, and 973 K. The cathodic current density and electrolysis time were 100 mA cm^{-2} and 10 min, respectively. The obtained Ti films at all temperatures have metallic luster. Especially, the sample at 823 K has high brightness with metallic luster. In addition, local depositions near the edge of the substrates due to the local concentration of current are observed at higher temperature. According to the surface SEM images, the grain sizes of the obtained Ti deposits increase with the temperature, for example, several micrometers at 823 K and around $30 \text{ }\mu\text{m}$ at 973 K.

The reason for the larger grain size at higher temperature is discussed with reference to the literatures. Wei *et al.* reported the same tendency in NaCl–KCl at 973–1123 K [8] and NaCl–KCl–LiCl at 773–923 K [9–12] with the addition of K_2TiF_6 and Ti metal powder. In these literatures, the larger grain size was explained by the increases of diffusion coefficient of Ti ions and diffusion rate of Ti atoms on the substrate surface. On the other hand, the author deduces that the recrystallization and grain growth of Ti are the possible reasons. Okazaki and Conrad reported the recrystallization and grain growth of Ti by vacuum annealing at 773–1073 K [13]. After annealing for 2 h, the grain size increased for the limit size of $1 \text{ }\mu\text{m}$ to 2–50 μm depending on the temperature. The grain sizes at 773 K and 973 K are approximately $2 \text{ }\mu\text{m}$ and $20 \text{ }\mu\text{m}$, respectively. Considering the reported results, the grain sizes of several micrometers at 823 K and $30 \text{ }\mu\text{m}$ at 973 K obtained by the electrodeposition in the present study are reasonably explained by the temperature dependent grain growth. Fig. 6-5 shows an illustration of a proposed model of Ti crystal growth during electrolysis. At 823 K, the maximum grain size is limited to be several micrometers. In contrast, at 973 K, deposited Ti can grow to a larger size of $30 \text{ }\mu\text{m}$.

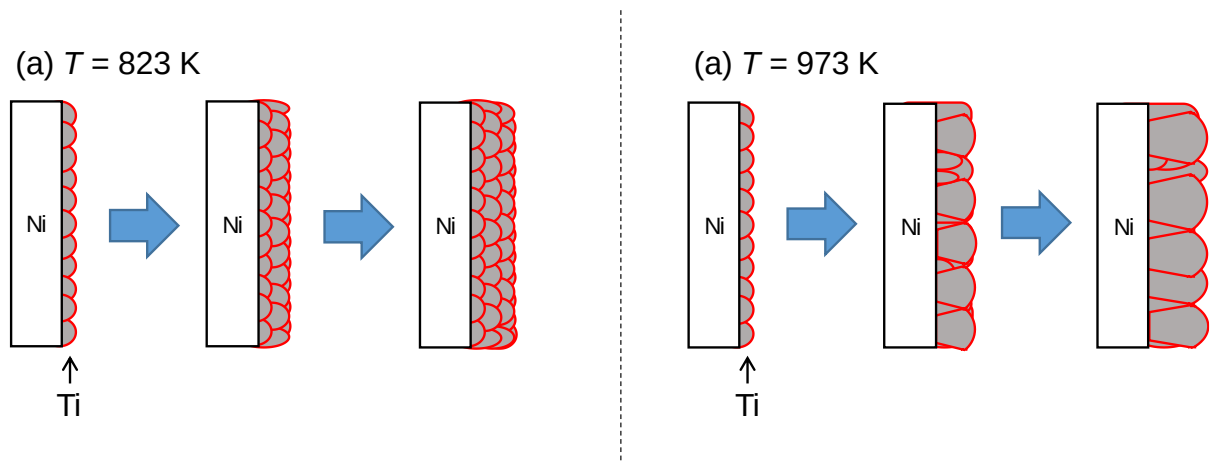


Fig. 6-5 An illustration of the model of crystalline grain growth during electrolysis at (a) 823 K and (b) 973 K.

Table 6-1 lists the surface roughness (S_a) measured for the samples shown in Fig. 6-4. The measurements were carried out in two ranges, (a) Narrow range: $401 \times 401 \mu\text{m}$ (area), $80 \mu\text{m}$ (cut-off length). (b) Wide range: $1.2 \times 1.2 \text{ mm}$ (area), $240 \mu\text{m}$ (cut-off length). The value of S_a increases with the increase of bath temperature. It should be noted that S_a at 823 K is especially small and almost the same with that of the original Ni substrate ($S_a = 1.2 \mu\text{m}$ for narrow range analysis). Ti films with smoother surface were successfully obtained at lower temperature by suppressing the grain growth of Ti.

Table 6-1 Surface roughness of the samples obtained at various temperature. Electrolysis conditions are the same as Fig. 6-4. The value is the average of 5 points. Narrow range: $401 \times 401 \mu\text{m}$ (area), $80 \mu\text{m}$ (cut-off length). Wide range: $1.2 \times 1.2 \text{ mm}$ (area), $240 \mu\text{m}$ (cut-off length).

		Bath temperature / K			
		823	873	923	973
Surface roughness (S_a) / μm	Measurement range				
	Narrow	1.12 ± 0.16	3.61 ± 0.29	3.78 ± 0.21	3.59 ± 0.35
	Wide	2.05 ± 0.22	4.58 ± 0.31	5.00 ± 0.65	5.71 ± 0.92

To obtain thicker films, longer-time electrolysis was conducted at 823 K. Fig. 6-6 shows the optical and SEM images of the samples obtained by galvanostatic electrolysis of Ni plates at 823 K. The cathodic current density was set to 50 mA cm^{-2} and the charge densities were set to 60, 150, and 450 C cm^{-2} . In the optical images, all samples have metallic luster though somewhat intensive local deposition is observed on the edges in the case of 450 C cm^{-2} . As shown in the cross-sectional SEM images, the thickness of Ti films increases up to $100 \text{ }\mu\text{m}$.

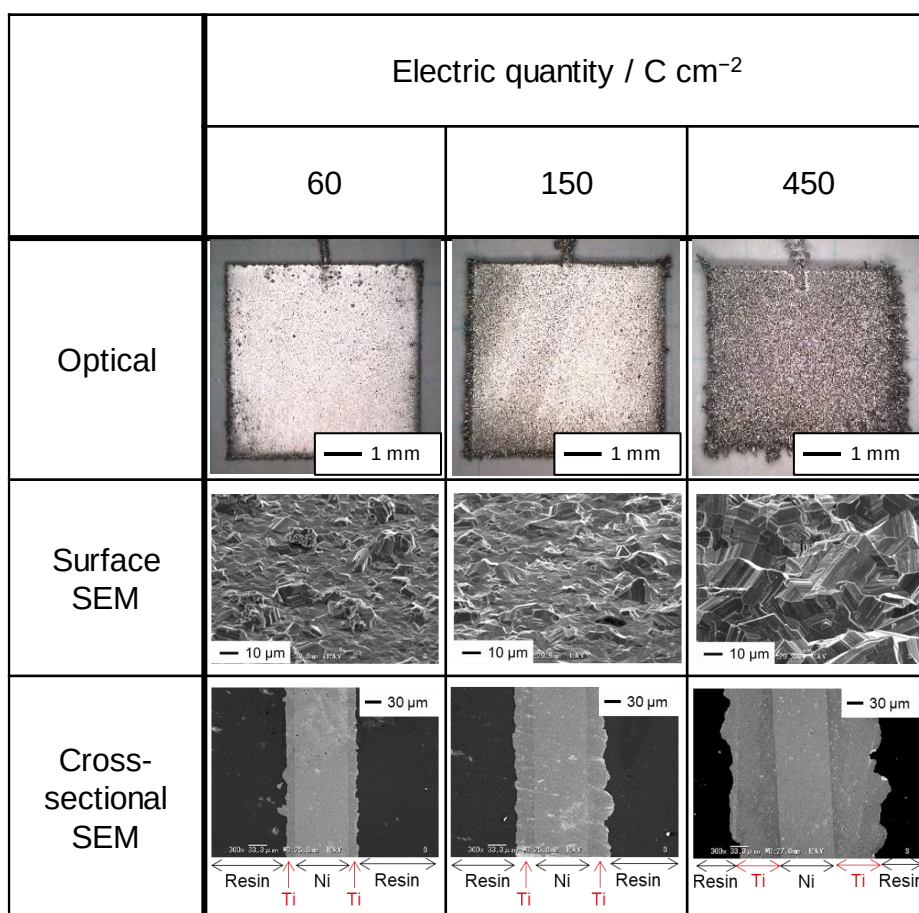


Fig. 6-6 Optical and SEM images of the samples obtained by galvanostatic electrolysis for Ni plates at a cathodic current density of 50 mA cm^{-2} in molten LiF-LiCl after the addition of Li_2TiF_6 (2.00 mol%) and sponge Ti (1.33 mol%) at 823 K. Charge density: 60, 150, and 450 C cm^{-2} .

6.4 Conclusion

The effects of temperature on the electrochemical behavior of Ti(III) ions and electrodeposition of Ti films were investigated in eutectic LiF–LiCl molten salt after the addition of Li_2TiF_6 and sponge Ti at 823–973 K. In cyclic voltammetry and square wave voltammetry, the reactions of Ti(III)/Ti(0) and Ti(IV)/Ti(III) were observed around 1.2 V and 2.8 V vs. Li^+/Li , respectively, at all temperatures. The diffusion coefficient of Ti(III) ions was given as a function of temperature by:

$$D_{\text{Ti(III)}} = 4.17 \times 10^{-3} \times 10^{-1.74 \times 10^3/T} (\text{cm}^2 \text{ s}^{-1}).$$

From the SEM observations and surface roughness measurements, Ti films having the smoothest surface were obtained at 823 K. Ti film with 100 μm thickness and relatively smooth surface was obtained at a current density of 50 mA cm^{-2} and a charge density of 450 C cm^{-2} at 823 K.

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Chapter 7

General Conclusion

The electrodeposition of Ti metal using fluoride–chloride molten salts consisting of single cations has been investigated with a purpose of expanding the use of metallic Ti. The factors to achieve compact and smooth Ti films were studied: such as Ti ion concentration, current density, and temperature in molten KF–KCl and LiF–LiCl. In particular, the effect of alkali metal cations on the electrochemical behavior of Ti(III) ions was investigated by comparing the results of KF–KCl and LiF–LiCl. The obtained results are summarized below.

In Chapter 2, the electrochemical behavior of Ti(III) ions and electrodeposition of Ti metal were investigated by cyclic voltammetry and galvanostatic electrolysis in eutectic KF–KCl after the addition of K_2TiF_6 (0.10 mol%) and an excess amount of sponge Ti at 923 K. The oxidation of Ti(III) ions to Ti(IV) ions was observed from 1.5 V vs. K^+/K in the positive scan for the voltammetry at a glass-like carbon electrode. The reduction of Ti(III) ions to Ti metal was observed at potentials more negative than 0.3 V. The solidified salt attached to the surface of the films was successfully removed by washing with water due to the high solubility of KF and KCl. XRD analysis revealed the deposition of crystalline metallic Ti films with high orientation to {101} plane. The Ti films had smooth surfaces and approximately 20 μm thickness.

In Chapter 3, more details of the electrochemical behavior of Ti(III) ions were investigated in KF–KCl molten salt after the addition of 0.50 mol% of K_2TiF_6 and 0.33 mol% of sponge Ti at 923 K. The cathodic reaction around 0.3 V vs. K^+/K was determined to be the reduction of Ti(III) ions to Ti metal by cyclic voltammetry, square wave voltammetry, and SEM/EDX and XRD analyses of the electrodeposits. The anodic reaction around 1.8 V in cyclic voltammetry was

confirmed to be a reversible electrochemical oxidation of Ti(III) ions to Ti(IV) ions. The concentration ratio of Ti(III) to Ti(IV) was calculated to be 4.6×10^6 from the measured rest potential (0.60 V) and the standard formal redox potential (1.82 V), which confirmed the completion of the comproportionation reaction. The diffusion coefficient of Ti(III) ions was determined by chronoamperometry as $3.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 923 K.

In Chapter 4, the optimal condition for the electrodeposition of adherent, compact, and smooth Ti films was investigated in KF–KCl–K₃TiF₆ at 923 K. The K₃TiF₆ concentration is used instead of the Ti(III) ions concentration in Chapter 4. The solubility of K₃TiF₆ was confirmed to be 1.48 mol% by ICP-AES analysis for the melts. Galvanostatic electrolysis was conducted on Ni plate substrates at various K₃TiF₆ concentrations (0.28, 0.70, and 1.43 mol%) and current densities (25–150 mA cm⁻²). The conditions to obtain adherent, compact, and smooth Ti films were determined to be 25–50 mA cm⁻² for 0.70 mol% K₃TiF₆ and 25–75 mA cm⁻² for 1.43 mol% K₃TiF₆. Moreover, linear sweep voltammetry in artificial seawater provided that the obtained Ti-coated Ni plate has no cracks and voids.

In Chapter 5, the effect of cations on electrochemical behavior of Ti(III) ions was investigated by using LiF–LiCl molten salt which has the same molar ratio of fluoride to chloride as the KF–KCl eutectic molten salt. After the addition of 0.50 mol% of Li₂TiF₆ and 0.33 mol% of sponge Ti at 923 K, the reduction of Ti(III) ions to Ti metal proceeds at around 1.2 V vs. Li⁺/Li, and a reversible electrochemical oxidation of Ti(III) ions to Ti(IV) ions occurs at 2.78 V. The diffusion coefficient of Ti(III) ions was determined to be $3.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ by cyclic voltammetry. The potentials for Ti(IV)/Ti(III) and Ti(III)/Ti(0) couples based on F₂/F⁻ potential in LiF–LiCl melt were 0.41 V and 0.31 V more positive than those in KF–KCl melt, respectively. Such potential differences are well explained by the interactions of Li⁺–F⁻ and K⁺–F⁻; the smaller cations interact more strongly with F⁻ and cause lesser stability of Ti(III) fluorocomplexes.

In Chapter 6, the effects of temperature on the electrochemical behavior of Ti(III) ions and electrodeposition of Ti films were investigated in eutectic LiF–LiCl molten salt after the addition

of Li_2TiF_6 and sponge Ti at 823–973 K. At all temperatures, the reactions of Ti(III)/Ti(0) and Ti(IV)/Ti(III) were observed around 1.2 V and 2.8 V vs. Li^+/Li , respectively. The diffusion coefficient of Ti(III) ions is given as a function of temperature by:

$$D_{\text{Ti(III)}} = 4.17 \times 10^{-3} \times 10^{-1.74 \times 10^3/T} (\text{cm}^2 \text{ s}^{-1}).$$

The surface SEM observations and surface roughness measurements for electrodeposited Ti showed that Ti films with the smoothest surface were obtained at 823 K. Ti film having *ca.* 100 μm thickness and relatively smooth surface was obtained at -50 mA cm^{-2} and a charge density of 450 C cm^{-2} at 823 K.

From the study on electrodeposition of Ti films in KF-KCl and LiF-LiCl , which are fluoride-chloride molten salts consisting of single cations, several advantages are found for practical applications. The molten KF-KCl has two features; one is the capability of electrodepositing adherent, compact, and smooth films, and the other is a washing easiness of solidified salts on the film surface. The molten LiF-LiCl has the important advantage of electroplating high-quality films with very smooth surface at a lower temperature. Since this special feature enables obtaining thick films with high quality, the molten LiF-LiCl is also expected to be applied for new processes of Ti smelting and recycling. Moreover, an academically important finding has been made; there is a large difference in the electrochemical behaviors of Ti(III) ions in KF-KCl and LiF-LiCl . The knowledge obtained in the present study, such as the roles of cations and anions in the electrochemical behavior of Ti(III) ions, will be both academically and industrially of use for further development in the field of molten salt chemistry.

Finally, the author expects that the wide-spread use of Ti metal will be achieved in the future.

List of Publications

The main parts of this thesis are constructed from the following papers.

Chapter 2

1. Yutaro Norikawa, Kouji Yasuda and Toshiyuki Nohira
“Electrodeposition of Titanium in a Water-Soluble KF–KCl Molten Salt”
Materials Transactions, **58**, 390–394 (2017).

Chapter 3

2. Yutaro Norikawa, Kouji Yasuda and Toshiyuki Nohira
“Electrochemical Behavior of Ti(III) Ions in a KF–KCl Eutectic Melt”
Electrochemistry, **86**, 99–103 (2018).

Chapter 4

3. Yutaro Norikawa, Kouji Yasuda and Toshiyuki Nohira
“Optimization of Electrolysis Conditions for Ti Film Electrodeposition from Water-Soluble KF–KCl Molten Salts”
Journal of the Electrochemical Society, **166**, D755–D759 (2019).

Chapter 5

4. Yutaro Norikawa, Kouji Yasuda and Toshiyuki Nohira
“Electrochemical Behavior of Ti(III) Ions in Molten LiF–LiCl: Comparison with the Behavior in Molten KF–KCl”
Journal of the Electrochemical Society, submitted.

Chapter 6

5. Yutaro Norikawa, Kouji Yasuda and Toshiyuki Nohira
“Effect of Temperature on Ti Electrodeposition in Eutectic LiF–LiCl Molten Salt”
Electrochimica Acta, to be submitted.

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March 2020

Yutaro Norikawa