ABSTRACT

The electrodeposition of titanium, in the low temperature molten electrolytes, has been studied by direct current and pulse current techniques. The morphology and composition of deposited layers were studied as a function of the electrolysis conditions. For example, the current forms, current density, pulse parameters, electric quantity and experimental temperature were examined. With increasing the current density, a decrease in crystal grain size was observed in both direct current and pulse current electrodeposition processes. The pulse current technique can be used to improve the Ti content of electrodeposited layers, especially in lower pulse current density. In the present study, the electrodeposited layer with 91.85% Ti content can be obtained by pulse current method.

From the results of study, it is concluded that a higher content of Ti electrodeposited layer can be obtained by the lower pulse current density with duty cycle of 75%, the low temperature molten electrolyte can be produced, and the feasibility of Ti electrodeposition from the low temperature molten electrolytes can be confirmed.

INTRODUCTION

The transition elements of group IVB to VIB of the periodic table are known as the refractory metals because of their high melting point and the favorable mechanical and physical properties at elevated temperature. Recently, they have become increasingly important because of the needs of the energy and aerospace industries for materials which will withstand extreme conditions, i.e., protecting metals against corrosion and high temperature oxidation.

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The titanium metal is an element of group IVB of the periodic table. It is very attractive material as surface coating with its special properties, e.g., good corrosion resistance and excellent mechanical properties. In particular, general corrosion, pitting and stress corrosion do not occur on titanium metal in the solution containing chloride ion(1). Therefore, it is the important one of refractory materials. The research of electrodeposition techniques of titanium on metal substrate for improving corrosion resistance have been drawing considerable attention(2-5).

From among the various methods of preparation of titanium film, such as CVD, PVD and electrochemical processes, the electrochemical deposition in ionic melts appears to be one of the most effective, as it makes it possible to deposite titanium films, depending on the composition of the electrolyte and the operating parameters of electrolysis, i.e., temperature, current density, current forms, etc.. Generally speaking, molten salts possess some unique properties, e.g., high conductivity, high current density and low vapor pressure, which facilitate efficient electrodeposition of metals. The high temperature molten electrolytes (generally above 650°C) employed in the electrodeposition of titanium film can essentially be divided into three groups, ① molten binary systems consisting of alkali chlorides mixture(6,7), ② alkali fluorides mixture, and ③ molten binary systems, consisting of alkali chloride-fluoride mixtures(8-12). Most of these systems, the corrosion problem is still exist owing to the high temperature operation. Thus, from the view point of energy conservation and cell materials corrosion problems, the solubility data of refractory metal compounds in the low melting molten salts have been drawing considerable attention. Such information is of critical importance to the technological development of these melts as electrolytes for lower temperature electrodeposition processes. However, the electrodeposition of titanium from lower temperature molten salts has still seldom been studied at present. Therefore, the techniques of electrodeposition of titanium metal from lower temperature molten electrolytes have a special significance in the field of surface coating technology.

In the present study, the lower melting molten salt electrolytes, i.e., the eutectic compositions of binary aluminum chloride-sodium chloride mixtures were selected and a new pulse electrodeposition technique was employed. One aim of the present study is to determined the solubility of $K_2TiF_6$ in low melting electrolytes solvent as the base of electrodeposition of titanium metal, another aim was to determine the influence of electrodeposition conditions on the quality of titanium deposited layer in such low melting electrolytes.

EXPERIMENTAL

586 Electrochemical Society Proceedings Volume 99-41
Electrodeposition of titanium metal in molten chloride salts electrolyte

Sodium chloride and potassium titanium fluoride were dried at 460 °C and 260 °C about 12 hours and 8 hours, respectively. This removed the residual moisture from these chemicals without further purification and then kept in desiccator. Aluminum chloride purified by twice sublimation and dried to remove residual moisture under vacuum at 105 °C. The appropriate amount of AlCl₃-NaCl-K₂TiF₆ mixture was transferred into a quartz container and placed in a reaction cell. The mixture was fused under vacuum and kept under a dry N₂ atmosphere.

The electrode assembly was composed of a nickel plate and titanium bar, which were used as a cathode and anode, respectively. The substrate of electrode was treated by mechanical polishing with SiC paper, then electropolished in acid solution with microcurrent. The polished surface was washed ultrasonically with distilled water, and then dried and cleaned with acetone.

Before the electrodeposition, pre-electrolysis was carried out to further purify the electrolyte, using the high quality aluminum plate as the two electrodes with microcurrent. The electrodeposition was conducted on the cathode with direct current and pulse current techniques at 170 °C and 190 °C, different quantity of electricity, current density and the ratio of on-time/off-time of pulse current, and carried out under the protection of a dehydrated high purity nitrogen atmosphere. The quantity of electricity for electrolysis was measured and displayed by electronic ampere-hour meter. The electrodeposited sample was washed with distilled water, cleaned in alcohol by using an ultrasonic cleaner, then dried and kept in a desiccator. The morphology of the electrodeposited sample was investigated by using scanning electron microscopy(SEM). The composition and identification of electrodeposited layers were examined by energy dispersive X-ray spectroscopy(EDX) and X-ray diffraction spectroscopy(XRD).

RESULTS AND DISCUSSION

Selection of electrolyte composition

In order to get the lower temperature molten electrolytes, we have tried to select the eutectic composition of binary ammonium formate-ammonium chloride mixtures, but the solubility of K₂TiF₆ in the mixtures is too low. The condition made the electrodeposition of Ti on Ni plate was bad. Therefore, it is important that selects the adequate electrolytes for obtaining good electrodeposition of titanium.

The aluminum chloride is a good solvent because it possesses the properties of acid and base. Most of the organic and inorganic chemicals can dissolve in it. It has a eutectic point at 108 °C with 40 mol% NaCl. Thus, the temperature of electrodeposition can be
reduced and the lower temperature electrolyte can be obtained. From the experimental results, we can know that the potassium titanium fluoride is slightly soluble into the binary molten salts. In order to obtain the better Ti electrodeposite, it is necessary to promote the concentration of titanium ions. Therefore, the composition of electrolyte selected as the molar ratio of AlCl₃60%-NaCl34%- K₂TiF₆6% for retaining the supplies of titanium ions in the electrolysis bath.

**Electrodeposition of titanium**

In order to investigate the effects of current forms and current densities, the electrodeposition of titanium in the molten electrolytes was carried out by the direct current densities range from 30 mA/cm² to 120 mA/cm² and by the pulse current densities range from 30 mA/cm² to 120 mA/cm² with two values of the ratio of the deposition time (t_{on}) to the rest time (t_{off}) were 3/1 and 1/3. The composition of electrodeposited layer was examined by EDX analysis. Fig.1(a,b) shown that the change in Ti weight percent of layers produced on Ni plate by electrodeposition with direct current density and pulse current density and the electric quantity at 3000 coulombs and 5000 coulombs. It is clear that current form had a pronounced effect on the composition of the titanium electrodeposited layer. The Ti content of electrodeposited layer from pulse current method was obviously higher than from direct current method. As for the effect of current density, it appears that an increase in Ti content with lower current density is systematically observed. On the other hand, the greater for the electric quantity, a higher Ti content of deposited layer is obtained.

The relationships between the grain size and the current density under the electric quantity of 3000 and 5000 coulombs are shown in Fig. 2(a,b). It is clear that current density had a obvious effect on the grain size of the titanium electrodeposited layer with dc and pc method. At the lower current density, due to the discharge of titanium ions occurred on the cathode slowly, thus the growth rate of nuclei exceeded the formation of new nuclei and the deposited Ti grains became bigger.

The SEM of the titanium electrodeposited layer under different current forms are shown in Fig.3(a,b,c). The result indicated that the grain homogeneity of deposited layer from direct current method was better than from pulse current method, but there was a higher Ti content of deposited layer for pulse current method. In the present study, the ratio of the deposition on-time to the off-time, t_{on}/t_{off}, was found to be an important factor in the morphology of deposited layer. Two values of the ratio:3/1 and 1/3 were chosen for electrodeposition and the frequency of the current wave form was kept constant. From Fig.3, the results indicate that the morphology and Ti content of electrodeposited layer from the ratio 3/1 were better than from the ratio 1/3.

Pulse current method has emerged as a new technique for the electrodeposition process(13,14). In the conventional dc electrodeposition, there is only one parameter,
namely, current density, which can be varied. However, in the pulse technique, an
unlimited number of combinations of different pulse current densities can be used for
obtaining a given average current density. It is well known that the electrodeposition rate
can be considerably increased during the on-time of pulse plating as compared to direct
current. For the pulse electrodeposition, it is well known that the crystallization of the
electrodeposited layer is very important step of the electrogrowth since it influences
directly the structure of the deposit and therefore its properties which represent the main
interest for the user. The crystallization is the process by which the adatoms or adions
incorporate in the crystal lattice. Crystallization occurs either by the build-up of old
crystals or the formation and growth of new ones. These two processes are in competition
and can be influenced by different factors. High surface diffusion rates, low population of
adatoms, and low overpotential are factors enhancing the build-up of old crystals, while
conversely low surface diffusion rates, high population of adatoms, and high
overpotential on the surface enhance the creation of new nuclei. In the pulse current
electrodeposition, since the pulse current density is usually considerably higher than the
corresponding direct current density, the population of adatoms on the surface during
pulse electrodeposition is higher than during direct current electrodeposition, resulting in
an increased nucleation rate and therefore in a finer grained structure and in higher Ti
content.

For understanding the effect of temperature to the pulse current method, the
electrodeposition of titanium in the molten electrolytes were carried out by the pulse
current at 190°C and the same duty cycle. From the composition analysis data of
electrodeposition layers by EDX shown in Table 1, it appears that the Ti content of
electrodeposition layers obtained at 190°C is higher than at 170°C. It is well known that
at the higher operating temperature, due to the transfer velocity of titanium ions moving
to the cathode increase, resulting in the more crystallizations and Ti contents. The SEM
photograph of Ti electrodeposition layer is shown in Fig.4. The morphology of Ti
deposition layer at 190°C was similar to at 170°C. On the other hand, the EDX and XRD
analysises of Ti deposition layers at 190°C were shown in Fig.5 and Fig.6, respectively.
The Ti content varied from 70.31% to 91.85% with decreasing the current density from
120mA/cm² to 30 mA/cm². From the XRD analysis, the existence of Ti content may be
confirmed further.

CONCLUSION

The electrodeposition of Ti from the low temperature molten electrolyte with direct
current and pulse current techniques was studied. The Ti content and surface morphology
of Ti/Ni layer were studied as function of the current forms, current density, pulse
parameters, electric quantity and experimental temperature. With increasing the current

Electrochemical Society Proceedings Volume 99-41
density, a decreased in crystal grains was noticed in both direct current and pulse current electrodeposition processes. The experimental results indicated that the Ti content of electrodeposited layer from pulse current method was obviously higher than from direct current method. So, the pulse current method can be used to improve the Ti content of electrodeposited layer, and an increase in Ti content with lower current density is systematically observed. On the other hand, the morphology and Ti content of electrodeposited layer from the ratio of $t_{on}/t_{off}$ 3/1 were better than from the ratio 1/3, and the Ti content of electrodeposited layers obtained at 190°C are better than at 170°C. In the present study, the electrodeposited layer with 91.85% Ti content can be obtained by pulse current method, and the XRD analysis can further confirm the existence of Ti content.

Taking into account all electrolytic conditions, it is concluded that a higher content of Ti electrodeposited layer can be obtained by the lower pulse current density with duty cycle of 75%. To sum up, the low temperature molten electrolyte can be produced, and the feasibility of Ti electrodeposition from the low temperature molten electrolytes can be confirmed.

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Table 1: Experimental conditions and results of analysis for Ti electrodeposition on Ni plate. (Preelectrolysis time=30 min)

| NO | Q (coulombs) | Electric current model | Temp (°C) | Current density (mA/cm²) | Time (hr) | Grain size (μm) | Ti (%) |
|----|--------------|------------------------|-----------|--------------------------|-----------|-----------------|--------|
| 1  | 5000         | D.C                    | 170       | 120                      | 3         | 0.8             | 5.23   |
| 2  | 5000         | D.C                    | 170       | 80                       | 5         | 1.0             | 18.41  |
| 3  | 5000         | D.C                    | 170       | 30                       | 12        | 1.7             | 29.27  |
| 4  | 5000         | Pulse(1:3)             | 170       | 120                      | 12        | 1.6             | 24.11  |
| 5  | 5000         | Pulse(1:3)             | 170       | 80                       | 20        | 1.8             | 37.17  |
| 6  | 5000         | Pulse(1:3)             | 170       | 30                       | 48        | 2.0             | 48.87  |
| 7  | 5000         | Pulse(3:1)             | 170       | 120                      | 4         | 3.0             | 66.36  |
| 8  | 5000         | Pulse(3:1)             | 170       | 80                       | 6         | 4.0             | 76.89  |
| 9  | 5000         | Pulse(3:1)             | 170       | 30                       | 16        | 5.0             | 89.14  |
| 10 | 5000         | Pulse(3:1)             | 190       | 120                      | 4         | 2.8             | 70.31  |
| 11 | 5000         | Pulse(3:1)             | 190       | 80                       | 6         | 4.0             | 80.13  |
| 12 | 5000         | Pulse(3:1)             | 190       | 30                       | 16        | 4.5             | 91.85  |
| 13 | 3000         | D.C                    | 170       | 120                      | 2         | 0.4             | 2.61   |
| 14 | 3000         | D.C                    | 170       | 80                       | 3         | 0.7             | 9.61   |
| 15 | 3000         | D.C                    | 170       | 30                       | 7         | 1.5             | 15.32  |
| 16 | 3000         | Pulse(1:3)             | 170       | 120                      | 8         | 0.5             | 13.65  |
| 17 | 3000         | Pulse(1:3)             | 170       | 80                       | 12        | 1.4             | 21.96  |
| 18 | 3000         | Pulse(1:3)             | 170       | 30                       | 28        | 1.8             | 28.49  |
| 19 | 3000         | Pulse(3:1)             | 170       | 120                      | 3         | 1.6             | 35.61  |
| 20 | 3000         | Pulse(3:1)             | 170       | 80                       | 4         | 2.0             | 51.98  |
| 21 | 3000         | Pulse(3:1)             | 170       | 30                       | 10        | 3.0             | 76.35  |
Fig. 1(a) Change in Ti weight percent of layers produced on Ni plate by electrodeposition with (a) direct current density $\downarrow$, (b) pulse current density $\Delta$, $t_{on}/t_{off} : 3 : 1$, (c) pulse current density $\blacksquare$, $t_{on}/t_{off} : 1 : 3$, at $170^\circ \text{C}$ with 3000 coulombs.

Fig. 1(b) Change in Ti weight percent of layers produced on Ni plate by electrodeposition with (a) direct current density $\downarrow$, (b) pulse current density $\blacksquare$, $t_{on}/t_{off} : 1 : 3$, (c) pulse current density $\Delta$, $t_{on}/t_{off} : 3 : 1$, at $170^\circ \text{C}$ with 5000 coulombs.
Fig. 2(a) Relationship between the grain size and the current density for the Ti electrodeposition at 170°C with 3000 coulombs. (a) direct current density ♦, (b) pulse current density ■, $t_{on}/t_{off}$ : 1 : 3, (c) pulse current density ▲, $t_{on}/t_{off}$ : 3 : 1.

Fig. 2(b) Relationship between the grain size and the current density for the Ti electrodeposition at 170°C with 5000 coulombs. (a) direct current density ♦, (b) pulse current density ■, $t_{on}/t_{off}$ : 1 : 3, (c) pulse current density ▲, $t_{on}/t_{off}$ : 3 : 1.
Fig. 3(a) Scanning electron micrograph of Ti electroplating layer
Temperature = 170°C
Direct current density: 120 mA/cm², 5000 coulombs

Fig. 3(b) Scanning electron micrograph of Ti electroplating layer
Temperature = 170°C
Pulse current density: 120 mA/cm², 5000 coulombs,
T_{on} : T_{off} = 1 : 3.
Fig. 3(c) Scanning electron micrograph of Ti electroplating layer
Temperature = 170°C
Pulse current density: 120 mA/cm² • 5000 coulombs,
$T_{on} : T_{off} = 3 : 1$. 

Fig. 4 Scanning electron micrograph of Ti electroplating layer
Temperature = 190°C
Pulse current density: 120 mA/cm² • 5000 coulombs,
$T_{on} : T_{off} = 3 : 1$. 

Electrochemical Society Proceedings Volume 99-41
Fig. 5  EDX spectrum of the Ti electroplating layer at 190°C
(a) Pulse current density, \( T_{on} : T_{off} = 3 : 1 \)
120mA/cm\(^2\), 5000 coulombs
(b) Pulse current density, \( T_{on} : T_{off} = 3 : 1 \)
80mA/cm\(^2\), 5000 coulombs
(c) Pulse current density, \( T_{on} : T_{off} = 3 : 1 \)
30mA/cm\(^2\), 5000 coulombs