THE ELECTROPLATING OF TITANIUM

FROM NaCl–KCl FUSED SALT

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ABSTRACT

The electrochemical reduction and electrodeposition process of titanium metal from NaCl–KCl molten salt have been studied by cyclic voltammetry and chronoamperometry. It has been confirmed that the reduction of Ti subchlorides are stepwise as: $Ti^{3+}+e=Ti^{2+}, Ti^{2+}+2e=Ti$ and electrochemically reversible. The diffusion of titanium ions is rate–controlling. The deposits of Ti have been found to partially diffuse into Pt or Fe substrates.

The electrodeposition of Ti metal undergoes instantaneous three dimensional nucleation nucleation and growth of hemispherical nuclei controlled by diffusion of ions in the melt. It could be used to optimise electroplating process of titanium. On this basis, high quality titanium coatings have been obtained by using the high frequency pulse potentiostatic technique.

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INTRODUCTION

Titanium and its alloys are widely used as important materials due to their high melting point, low specific gravity, corrosion resistance and high strength. Electroplating of titanium onto various substrates may offer combined properties of Ti and substrate materials. Hence the electroplating of Ti is an efficient method to more effectively utilize Ti metal. Recent studies have dealt with electrodeposition of Ti from molten salts because Ti could not be deposited from aqueous solutions. Electrodeposition processes in molten salts are generally rate–controlled by diffusion of ions and result in dendritic deposits. The practical experience of molten salt electroplating shows: Due to the influence of concentration polarization, the irregular profile produced is unavoidable in molten salts electroplating under constant current density(1). In molten salt electroplating, it is hard to find the complex smoothing and leveling agents which may be used to control the quality of coated layers. Thus, operation under charge–transfer (kinetic) control, or control of initial stage of nucleation and growth may be a prerequisite for obtaining coherent deposits of Ti metal(8).

The present investigation was undertaken to determine how far cathodic reduction of Ti ions occurs, and to characterize the nature of electrodeposition of Ti metal from NaCl–KCl(1:1mol%) molten salt by cyclic voltammetry and chronoamperometry. Based on these studies, it is easy to find out the relation of the forms and properties of titanium deposits prepared under well defined electrochemical conditions, and use this to optimise the properties of electroplate.

EXPERIMENTAL

Experiments were performed in a stainless steel cell. The NaCl and KCl salts used were of analytical purity. The electrolyte NaCl–KCl (1:1mol%) was contained in an inner alumina crucible and dehydrated under vacuum prior to use as temperature was gradually raised to 480°C, then the mixture continued to be melted at 720°C under an argon atmosphere. It was followed by preelectrolysis using a graphite rod electrode until the residual current was less than $0.5\text{mA} / \text{cm}^2$. Titanium subchlorides were prepared by the reaction of Ti metal with liquid titanium tetrachloride in a NaCl melt at 700°C.

The potentiostatic circuit consisted of a three–electrode system, Potentiaostat SHD–1, and an XY recorder. The reference electrode was Ag / AgCl–(NaCl–KCl)(1) which was shielded from the electrolyte by a porcelain sheath. The working electrode was a Pt flag or a pure iron sheet, and the counter electrode was a graphite rod. A Pt wire and low carbon steel wire were used as working electrode, pure titanium sheet as a counter electrode, and a Ti wire as reference electrode during chronoamperometric experiments. Because of disproportionation of Ti subchlorides, electrochemical measurements should be carried out after the establishment of equilibrium between Ti metal, Ti^{2+} and Ti^{3+}, which was determined by measuring the electrode potential(1) $E_{Ti^{2+}/Ti^{3+}}$ vs. Ag / Ag(I) reference potential.

In electroplating, the working electrode is made of low carbon steel wire, the counter electrode is a pure titanium plate, and the reference electrode is of a pure titanium wire. A Mo rod was used as an indicating electrode, an Ag / AgCl for the reference electrode, for measuring the average valance of the system. The low carbon steel rod used as the substrate of electroplating must be polished in a stepwise fashion using metallographical sand–paper of different grades.

The electrolyte NaCL: KCL (1:1 mol) containing low–valance titanium salt, (under sat. Ti sponge conditions) is maintained for 4 hours to achieve equilibrium. When the average valance falls below 2.35, the electroplating can proceed. At this point, the electrolyte contains 4.4 wt% $TiCl_2$ and 2.0 wt% $TiCl_3$.

RESULTS AND DISCUSSION

The Study of Electrochemical Process

Fig.1 represents typical voltammogram obtained after addition of Ti subchlorides to the NaCl–KCl melt. There are two reduction waves (a,b) and three reoxidation waves (c, d, and e) when the potential scan is reversed.

Peak potentials E_p^a *and* E_p^b, and half–peak potentials $E_{p/2}^a$ *and* $E_{p/2}^b$, are virtually unchanged with increasing scan rate v, indicating that both reduction processes are reversible(2–3). The cathodic current peaks I_p^a and I_p^b increase linearly with an increase in (scan rate)$^{\frac{1}{2}}$ at various concentrations as shown in Fig.2. Both reduction processes are diffusion–controlled(4).

A half–peak potential for a soluble product under reversible condition is given by the equation:

$$E_{p/2} - E_p = 2.20RT / nF \tag{1}$$

According to equation (1), electron numbers n_a and n_b of electrode reactions for Ti^{2+} and Ti^{3+}, respectively, were calculated as $n_a = 1.27$ *and* $n_b = 2.07$. The results show that cathodic reduction of Ti subchlorides undergoes two steps: $Ti^{3+}+e=Ti^{2+}$ and $Ti^{2+}+2e=Ti$. The deposition titanium metal can dissolve into the Pt substrate and form a Ti–Pt alloy.(5).

Typical current–time transients obtained for electrodeposition of Ti onto Pt electrode is presented in fig.3. The currents did not simply decay with time, but increased again after rapidly decreasing. This is characterisitic of nucleation and growth of nuclei.

The I VS. $t^{\frac{1}{2}}$ relationship corresponding to rising sections of current–time profiles under various overpotentials shows linear dependence with increasing slopes(fig.4). It obeys the kinetic equation for instantaneous nucleaction(6,7)followed by growth of three dimensional nuclei under ions mass–transfer control:

$$i = ZF\pi N_0 (2DC)^{\frac{3}{2}} M^{\frac{1}{2}} t^{\frac{1}{2}} / \rho^{\frac{1}{2}} \tag{2}$$

where ZF is the molar charge of depositing species, D is its diffusion coefficient, C its concentration in mol cm^{-3}, M its molecular weight and ρ its density. Hence, the electrodeposition of Ti onto Pt electrode presents instantaneous nucleation features. The slopes of $I - t^{\frac{1}{2}}$ lines increases with increasing overpotentials and indicates that nucleation rate and nucleation densities are very sensitive to the magnitude of overpotentials, Nucleation densities increase with increasing overpotential, and the crystallites become finer.

This chronoamperommetry study reveals that electrodeposition of titanium undergoes an initial stage of nucleation and growth of nuclei under proper overpotentials. Therefore, it is possible to obtain the maximum nuclei density by controlling overpotentials in order to produce a coherent, dense and adherent deposit of Ti metal.

The Electroplating of Titanium

a. Constant Potential Electroplating

The constant potential electroplating means an over potential is continuously maintained during the process of electroplating. The results from investigating of electrodeposition show that it is the same for the Ti deposition as that for other metals, and that a critical nucleation overpotential exists. The constant potential must be higher than the critical nucleation potential.

The metallograph shows that if the overpotential is under constant potential electroplating, a branch style crystal is observed. If it is cleaned by dilute sulphuric acid, the loose branch style crystals will be lost, in which only a thin uniform layer near the substrate is left, as shown in Figure 5. The thickness of the coated layer abtained from the process of constant potential method is rather thin ($5 \sim 6\mu$).

b. Pulse Potential Electroplating

Two types of pulse electroplating have been used. One is with low frequency pulse, or in other words, the time interval for nucleation is about several seconds. The other is with higher frequency, that is 10^{-2}–10^{-4}sec.for nucleation.

1. Low Frequency Pulse Electroplating

After each nucleation, the potential on electrode drops to zero (relative to Ti reference electrode), hence no nucleation occurs on the electrode. about 20mA dissolving current is proceeded, the concentration of Ti ions on the surface of electrode is increased, this will be benificial to the nucleation for the next pulse. After the pulse sustains a period, the layer near the substrate with partial branch style crystal components evidently reduces, and the rate of covering is increased clearly (Fig.6). In low frequency pulse electroplating, when $\eta_1 = -350$ to -500mv, t = 2sec. or 3sec, $\eta_2 = 0$, the time for on and off ratio $t_1 / t_2 = 2:1$ or 1:1, and after several pulses, the coated layer on the substrate has rather good cohesion and high covering rate.

2.Higher Frequency Pulse Electroplating

Many papers indicate that pulse electroplating can produce high quality coating which are much better than those from direct current electroplating. Not only is the crystallization of the coating fine, the grain of crystal small, and the holes on the coating reduced, but also impurities in the coating largely reduced. Thus, the purity of the layer is enhanced, and corrosion resistance is improved.

In our experiments, square–wave voltage pulses are used, in which t_1 *and* t_2 are all in the range of 10^{-2}–10^{-4}sec.. Fig.7 shows that the good covering rate and fine structure of the coating can be obtained near the substrate under conditions of: $\eta_1 = -350\sim-500$mv,$\eta_2 = 0$, $t_1 = 10^{-2}$–10^{-4}sec, and an on / off ratio t_1 / t_2= 1:1: or 2:1.

The Characteristics of Coating

The covering rate of a coating is the criteria of the quality of the layer. Fig.8, which corresponds to Fig.7 represent the topographs of coatings. These pictures show that the grain sizes on the surface are uniform, no holes are present and a better covering rate was achieved. The energy spectrum obtained from a scanning electromicroscope indicated that the coating is pure Ti metal. (Figure 9).

CONCLUSIONS

1. The electrolytic reduction process of titanium ions in NaCl–KCl melt, at 720℃, has been studied by cyclic voltammetry. The results indicate that the cathodic reduction of Ti(Ⅲ) and Ti(Ⅱ) are Ti(Ⅲ)+e = Ti(Ⅱ) and Ti(Ⅱ)+2e = Ti, and both reductions are diffusion controlled.
2. The electrocrystallization of titanium has been studied by chronoamperometry. The chronoamperogram showed that the deposition process of Ti involves instantaneous three dimensional nucleation followed by growth of nuclei contolled by diffusion of ions in the melt.
3. The method of constant potential or the method of pulse electroplating can produce a fine structure Ti coating on low carbon steel substrate for NaCl–KCl (1:1 molar radio) molten salt system under 700℃. The stability of the experiment, the uniformity of the coating, and the covering rate obtained by the pulse electroplating are better than those associated with the constant potential method. Fine structure crystals can be achieved at the beginning stage of nucleation in NaCl–KCl–4%$TiCl_2$–2.2% $TiCl_3$ at 700℃ under the following two sets of conditions.

   a.low frequency

   $\eta_1 = -350\text{mv}\sim-500\text{mv}$, $\eta_2 = 0$, $t_1 = 2$–3sec, and t_2 / t_1 = 1:1 or 1:2.

   b.higher frequency

   $\eta_1 = -350\text{mv}\sim-500\text{mv}$, $\eta_2 = 0$, $t_1 = 10^{-2} - 10^{-4}$ sec, and t_2 / t_1 = 1:1 or 1:2.

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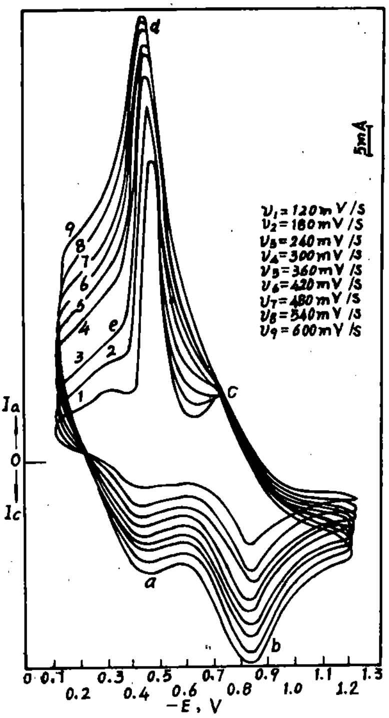

Fig.1. Typical Voltammogram obtained using a Pt electrode ($A = 0.24 cm^2$) $TiCl_2 = 0.70\%$ wt, $TiCl_3 = 0.44\%$ wt.

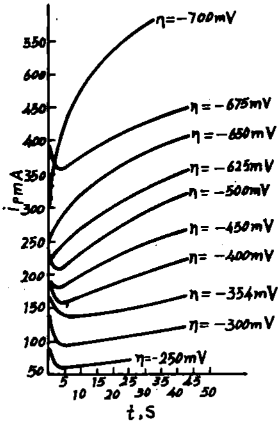

Fig.3. Chronoamperograms for the reduction of titanium ions in NaCl–KCl at 700℃ ($TiCl_2$ 4.0%wt, $TiCl_3$ 2.2%wt, Pt electrode, S = 0.016cm, vs. Ti^{+2}/Ti^{+3})

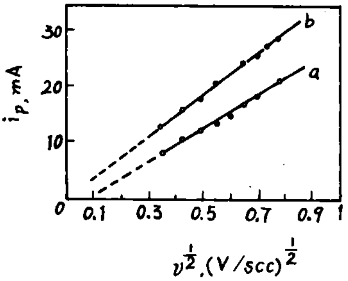

Fig.2. Plots I_p^a, $I_p^b - v^{1/2}$(Pt electrode)

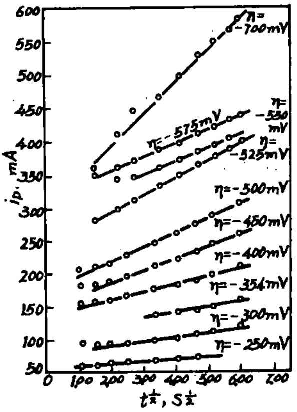

Fig.4. I_p vs. $t^{1/2}$ plots for the growth of titanium nuclei on a Pt electrode.

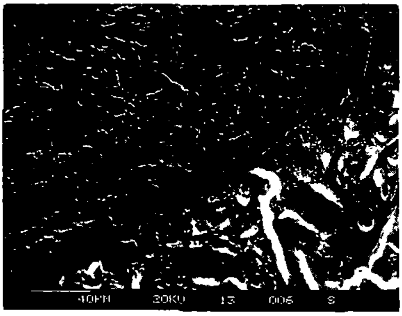

Fig.5. Transverse section of Ti coating (375x), constant potential electroplating. $\eta_1 = -300$mv, t = 10min.

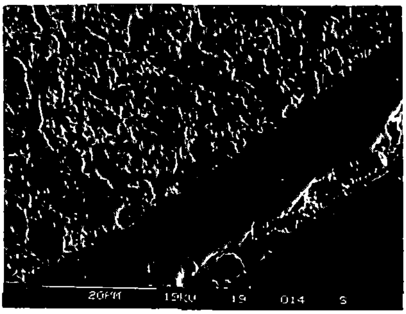

Fig.6. Transverse section of Ti coating (1400x) Low frequency pulse electroplating. $\eta_1 = -400$mv, $\eta_2 = 0$. $t_1 = 3$ sec, $t_2 = 1$ sec.

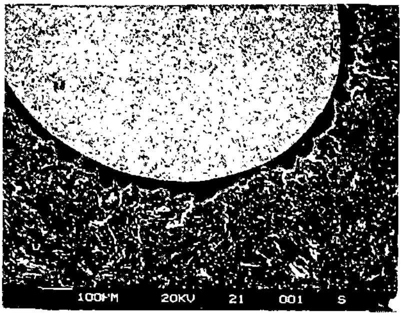

Fig.7. Transverse section of Ti coating (100x) High frequency elctroplating $\eta_1 = -350$mv, $\eta_2 = 0$, $t_1 = 3 \times 10^{-4}$sec, $t_2 = 2 \times 10^{-4}$sec. Electroplating time 30 min.

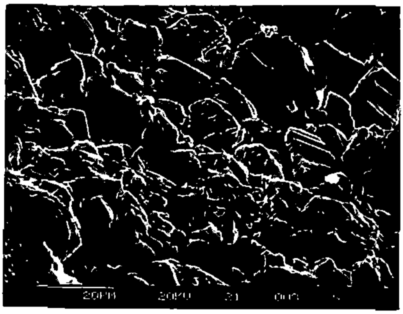

Fig.8. Topograph of coating (1100x)

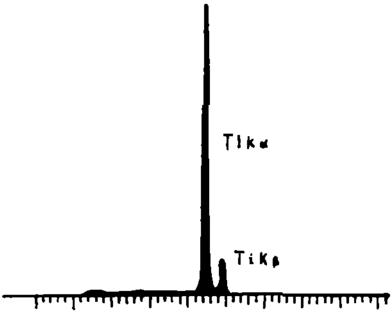

Fig.9 Energy spectrum of the coating surface