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Characteristics of titanium deposits by electrolysis in molten chloride–fluoride mixture

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Titanium deposits were prepared on 304 stainless steel substrates by both constant current and pulse current methods in molten KCl–NaCl–LiCl eutectic salts with 2 mol % potassium hexafluorotitanate. The influence of electrolysis conditions on the crystal orientation and morphology of the titanium deposits was investigated by using X-ray diffraction and scanning electron microscopy, respectively. It was found that the orientation index of the titanium deposits varied with temperature, electrolysis time, current density and pulse shape during electrolysis. The deposits showed a granular structure, in which the grains became larger with increase in temperature. Titanium deposits with pulse current above 873 K had a better corrosion resistance than pure titanium sheet.

1. Introduction

The electrodeposition coatings of refractory metals from molten salts is a promising surface modification method for protecting substrate materials against corrosion and high temperature oxidation [1–4]. For instance, the electrodeposition coatings of refractory metals such as chromium, niobium, tungsten and titanium on the surface of ferrous materials facilitates their use in extreme environmental conditions. However, these pure refractory metal compounds usually exhibit high volatility and disproportionation chemistry [5], so that it is difficult to prepare pure refractory metal coatings electrolytically from molten salts.

Among these metals, titanium is appropriate for refractory metal coatings due to its favourable properties such as high strength-to-weight ratio, inertness to many corrosive environments and its abundant reserves. As a result, much work has focused on the electrochemical behaviour and electrodeposition of titanium in molten chloride, fluoride and chloride–fluoride mixed electrolytes [6–19], although information regarding the electrodeposition coating technique and growth mechanism of titanium deposition is sparse. Little literature exists on the morphology and crystal orientation of adherent titanium deposits from molten salts. Vargas and Inman [20], in their study of chromium electroplating from molten KCl–LiCl mixtures, demonstrated that electrocrystallization may be controlled by using different potential functions. Pulse electrolysis helps to avoid concentration polarization and is suitable for obtaining compact and adherent deposits.

Studies on some characteristics of titanium deposits in molten KCl–NaCl–LiCl eutectic salt containing 2 mol % potassium hexafluorotitanate, K_2TiF_6, are presented in this paper. The crystal orientation and the morphology resulting from electrolysis under conditions such as different temperature, different electrolysis time and different current type, were characterized by X-ray diffraction analysis (XRDA) and scanning electron microscopy (SEM). In addition, the corrosion resistance of titanium deposits was evaluated by means of measurement of current/potential curves in 3% NaCl solution.

2. Experimental details

2.1. *Electrolytic cell*

The electrolysis cell is shown schematically in Fig. 1. Experiments were performed under an inert argon atmosphere at temperatures of 723–923 K. The variation of temperature was controlled within ±1 K. The sealed reaction chamber was made of a quartz container sealed at the top by a silicone rubber stopper which also held the electrodes and the thermocouple. An alumina crucible (SSA-S, Nippon Kagaku Tokyo Co., Ltd) was used to hold the molten electrolytes.

2.2. *Preparation of the molten salt*

KCl–NaCl–LiCl (38 mol %–10 mol %–52 mol %) eutectic salt was used as the supporting electrolyte. This mixture was prepared from alkali halides of reagent grade dried at 473 K for 86.4 ks, and heated to the melting point under an argon atmosphere. 2 mol % K_2TiF_6 (assay: minimum 98%) was then added to the supporting electrolyte melt. A pre-electrolysis treatment was carried out for 172.8 ks by using auxiliary electrodes (titanium rod served as anode) at 873 K at a very low current density ($50\,\mathrm{A\,m^{-2}}$) to remove moisture, metallic impurities and oxides as far as possible.

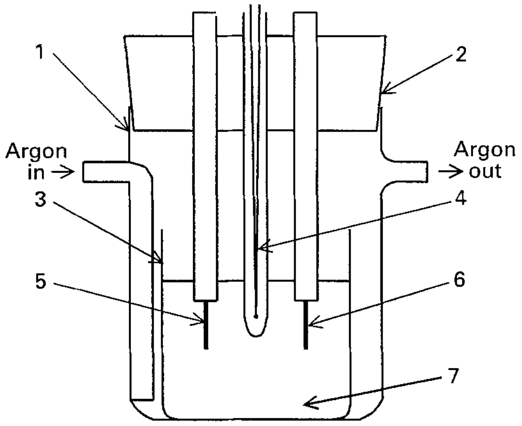

Fig. 1. Electrolysis cell. (1) Quartz vessel, (2) silicone rubber, (3) alumina crucible, (4) thermocouple, (5) working electrode, (6) counter electrode and (7) molten salts.

2.3. *Electrodes*

The cathode was a 304 stainless steel sheet of approximately 2 cm^2 area, which was polished and then rinsed with acetone prior to electrolysis. The anode was a titanium rod of 1 cm diameter (purity: 99.5%).

2.4. *Electrolysis and analysis of deposited titanium*

Electrodeposition was carried out with both constant current and pulse current. The pulse current shape is schematically shown in Fig. 2, where the parameters are as follows: $I_1 = -4500\,A\,m^{-2}$; $I_2 = -2000\,A\,m^{-2}$; $I_3 = +500\,A\,m^{-2}$; T_1:T_2:T_3 = 1:8:1; and pulse period, $T_p = 5$ s. Titanium deposits were prepared under different conditions of varying temperature, electrolysis time and a current density, I_2, in the case of pulse current electrolysis. After electrolysis, the cathode was lifted above the bath level for draining, and removed from the chamber, washed in water with ultrasonication, rinsed with acetone and dried. To observe the cross-section of titanium deposits, specimens were bent in liquid nitrogen until fractured. The deposits were analysed by scanning electron microscopy (Hitachi S-800) and X-ray diffraction (Rigaku-denki, RINT1500) to obtain information on surface morphology and preferred crystal orientation, respectively. Here, the orientation index was estimated by using the Wilson equation [21] as follows:

$$\text{Orientation index} = \frac{I_{(hkl)}/\sum I_{(hkl)}}{I_{\mathrm{ASTM}(hkl)}/\sum I_{\mathrm{ASTM}(hkl)}} \qquad (1)$$

Where $I_{(hkl)}$ is the integrated intensity from an (hkl) peak, and $I_{\mathrm{ASTM}(hkl)}$ is the intensity of the (hkl) peak obtained from an ASTM card corresponding to a random texture. If the orientation index of (hkl) is unity or less than unity, it is considered that that (hkl) face has no preferred orientation. The high orientation index means that its crystal face lies parallel to the substrate surface.

The measurement of current/potential curves of the deposits was conducted at a potential sweep rate of $4\,mV\,s^{-1}$, after specimens were held for 600 s at their rest potential in 3% NaCl solution at room temperature.

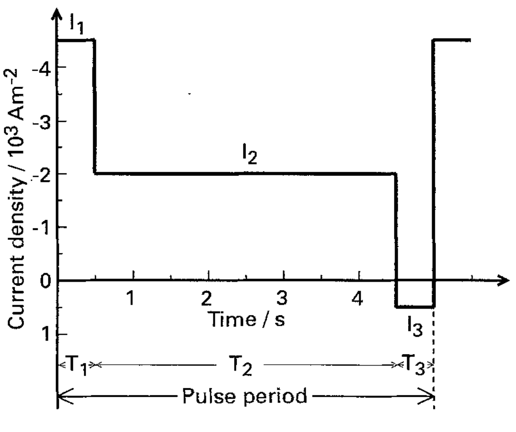

Fig. 2. Schematics of the pulse current used in the electrolysis.

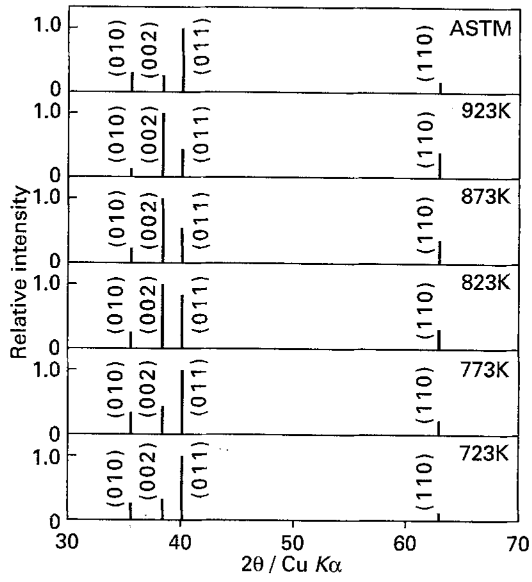

Fig. 3. X-ray diffraction patterns of titanium deposits with constant current.

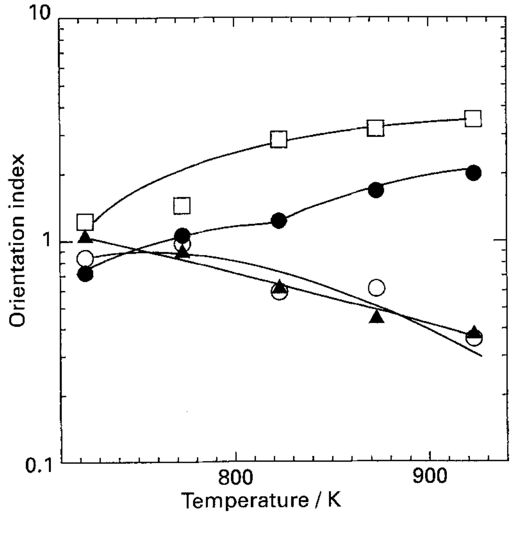

Fig. 4. Effect of temperature on the orientation index of titanium deposits for 3.6 ks with constant current ($-2000\,A\,m^{-2}$) in KCl–NaCl–LiCl + 2 mol% K_2TiF_6. ●: (1 1 0), ○: (0 1 0), □: (0 0 2), ▲: (0 1 1).

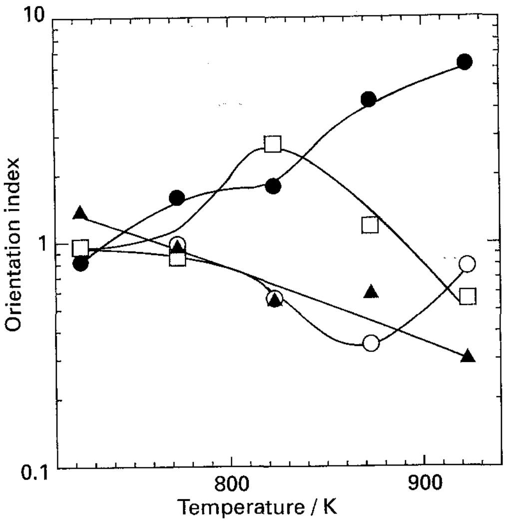

Fig. 5. Effect of temperature on the orientation index of titanium deposits for 3.6 ks with pulse current in KCl–NaCl–LiCl + 2 mol % K_2TiF_6. Indices as in Fig. 4.

3. Results and discussions

3.1. *The effect of electrodeposition temperature*

3.1.1. Crystal orientation. The effect of temperature on the crystal orientation of titanium deposits was examined under electrolysis with both constant current and pulse current. The relation between temperature and crystal orientation of the deposits at a current density of 2×10^3 A m^{-2} with constant current is shown in Fig. 3. The orientation indices calculated by Equation 1 are shown in Fig. 4. It can be seen that the crystal orientation index of the deposits varied with temperature. Titanium deposits prepared at temperatures up to 773 K had a random texture, as all the orientation indices were approximately equal to one. At temperatures above 773 K, the deposits tended to show (0 0 2) and (1 1 0) preferred orientations. In contrast, the orientation index of (0 1 1) decreased as temperature increased.

Figure 5 shows the orientation index of the deposits at various temperatures under the pulse current electrolysis. Although the deposit below 773 K had a random texture similar to those shown in Fig. 4, it showed (1 1 0) preferred orientation above 873 K.

As for the change in the preferred orientation of the deposits, it is essential that the nonequilibrium growth of titanium adatoms on the growing surface result in the change of orientation during electrodeposition. Generally, the difference in growth rate on each crystal plane is expected to be small at low temperature and large at high temperature [24]. It can be also controlled by adsorption of foreign species, because their adsorption may also change the growth mechanism. The inhibition effect of additives such as brighteners has been reported during electroplating in aqueous solution [25]. In addition, Oki and Wang [26] attempted to analyse the preferred crystal orientation of some thin films deposited by ion plating. The difference in growth rate was due to the deposition being inhibited by adsorption of foreign species.

Titanium has a close-packed hexagonal structure (h.c.p.) and the relative order of surface free energy, $\gamma_{(hkl)}$, is represented as $\gamma_{(011)} < \gamma_{(002)} < \gamma_{(110)}$ [23]. When the titanium was electrodeposited at lower temperature such as 723 and 773 K by constant current and pulse current, the nuclei grew at random. Thus, the deposits exhibited a random texture with fine grains. As temperature increased further, the deposits with constant current showed (0 0 2) preferred orientation, and those with pulse current exhibited (1 1 0). This implies that the (1 1 0) and (0 0 2) faces grow slowly and remain; this may be caused by the inhibition effect of foreign species on the crystal planes with higher surface free energy. It appears that pulse current affects the structure of the electrical double layer and the mechanism of electrocrystallization, so that the orientation of the deposits under pulsed current differ from those under constant current. The difference in crystal orientation between constant current and pulse current, particularly at high temperature, is also influenced by the applied deposition overpotential. The overpotential at constant current, which corresponds to the I_2 value in pulse current, was −0.25 V. The overpotential in pulse cur-

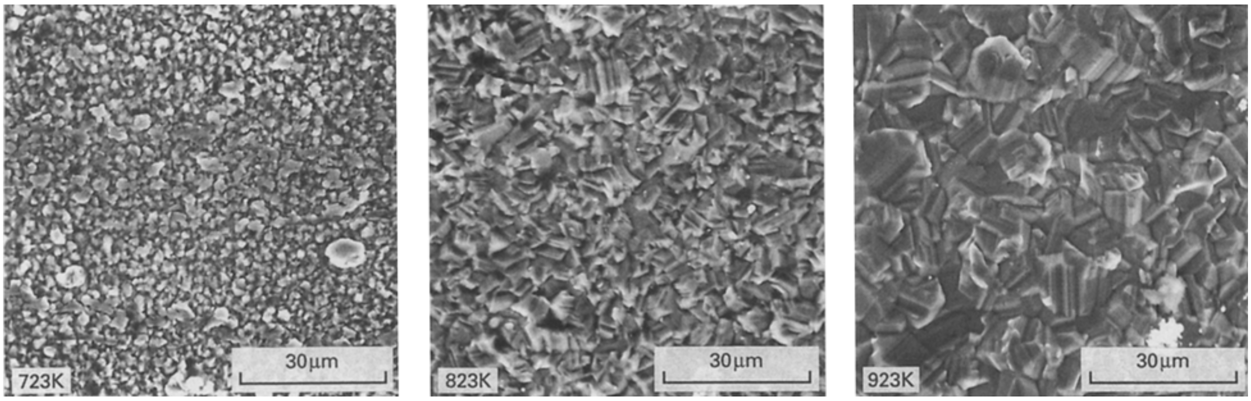

Fig. 6. SEM micrographs of the surface of titanium deposits for 3.6 ks with constant current (−2000 A m^{-2}) in KCl–NaCl–LiCl + 2 mol % K_2TiF_6.

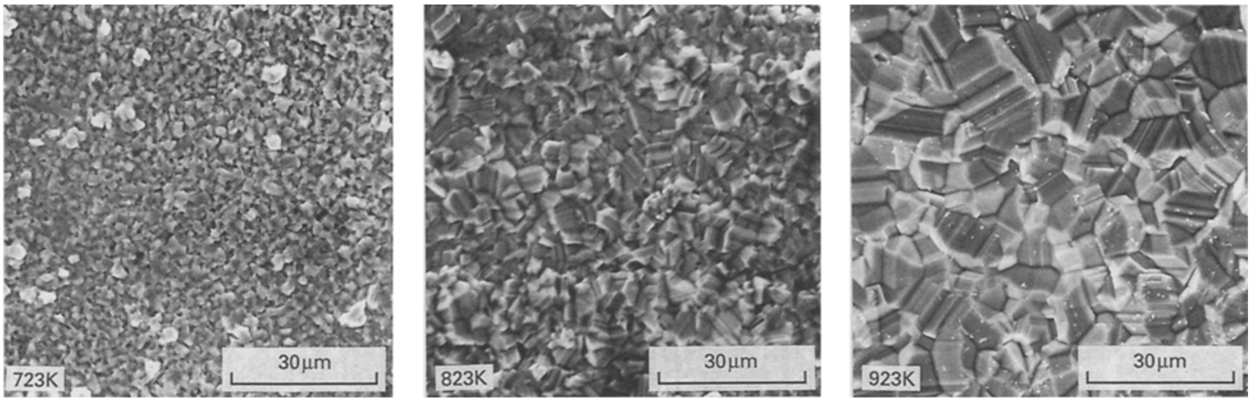

Fig. 7. SEM micrographs of the surface of titanium deposits for 3.6 ks with pulse current in KCl–NaCl–LiCl + 2 mol % K_2TiF_6.

rent, I_1, was −0.5 V. Therefore, the large current over the pulse period, T_1, affects the crystal orientation.

3.1.2. Surface morphology. Photographs of the surface of titanium deposits prepared at constant current of $-2000\,\mathrm{A\,m^{-2}}$ are shown in Fig. 6. The deposits in the temperature range of 723–923 K exhibited a granular structure. The surface morphology of the deposits changed with temperature, i.e. the grains became larger with increasing temperature. They were composed of well-crystallized grains [22], whose nuclei grew with regular geometries above 823 K. The photographs of titanium deposits obtained with pulse current are shown in Fig. 7. It was found that the surface morphology of the deposits also varied with temperature, but the grain shapes by pulse current were more clear than those by constant current. The deposits by pulse current had excellent homogeneous and smooth surfaces macroscopically, because a low anodic current period of pulse current improves the homogeneity and smoothness of the deposits owing to prior dissolution of the grain tips. The deposits became lustrous with a silver-grey appearance when deposited above 823 K.

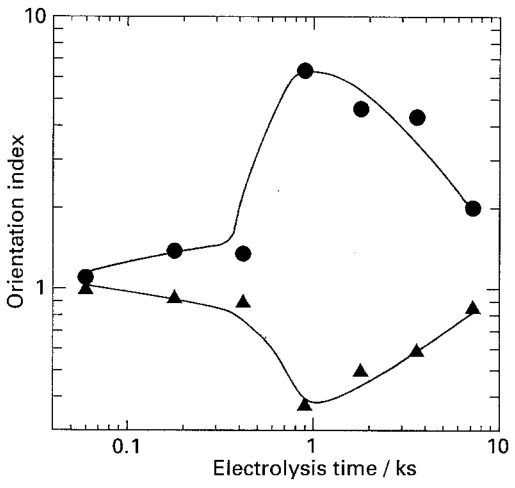

Fig. 8. Effect of electrolysis time on the orientation index of titanium deposits with pulse current at 873 K in KCl–NaCl–LiCl + 2 mol % K_2TiF_6. ●: (1 1 0), ▲: (0 1 1).

Titanium deposits were granular, not dendritic. Thus, the nuclei do not grow in the form of dendrites over a certain concentration of solute if current density is not very high. This agrees with the fact that a high solute concentration results in a high limiting current and a relatively larger current range is available for deposition without dendrite formation. The conventional process of electrocrystallization in molten electrolytes appears to be diffusion controlled so that the deposits often tend to form dendrites at high current density. In pulse electrolysis, it may be easier to prepare compact, dense and adherent deposits because concentration polarization can be minimized by use of pulse current.

3.2. *The effect of electrodeposition time*

The relation of the preferred orientation and morphology of the deposits with time was explored. The orientation index of the deposits obtained using pulse current at 873 K is shown in Fig. 8. It was found that the deposits had a random texture up to 420 s. With electrolysis within 0.9 to 7.2 ks, the deposits exhibited a (1 1 0) preferred orientation. The orientation index of (1 1 0) rapidly increased up to 0.9 ks, and then decreased with time. The change in the orientation index of (0 1 1) was opposite to (1 1 0). The

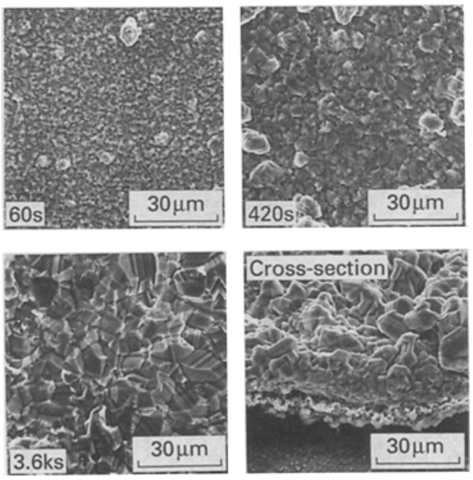

Fig. 9. SEM micrographs of the surface of titanium deposits with pulse current at 873 K in KCl–NaCl–LiCl + 2 mol % K_2TiF_6.

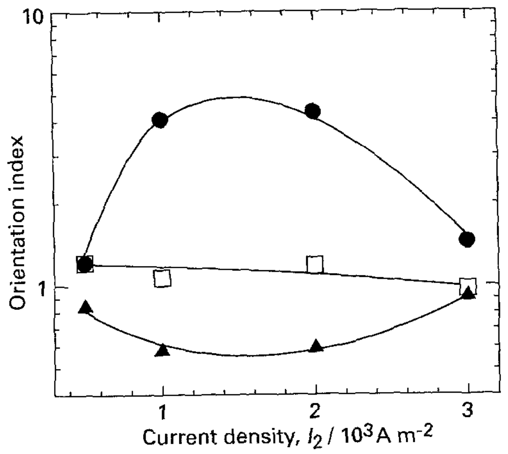

Fig. 10. Effect of current density of I_2 on the orientation index of titanium deposits with pulse current at 873 K for 3.6 ks in KCl–NaCl–LiCl + 2 mol % K_2TiF_6. ●: (1 1 0), ▲: (0 1 1), □: (0 0 2).

orientation index of the other face was not shown because of no distinct change in it. Because the 304 stainless steel substrate was polycrystalline, the nuclei formed would be random at an early growth stage. Consequently, the orientation depended on the preferred growth from the initial nuclei. During the initial electrocrystallization, the deposits showed random texture with fine grains due to random nuclei formation. As the electrodeposition continued, the deposits exhibited some preferred orientation due to non-equilibrium crystal growth. This agrees with previous work on titanium deposition from NaCl–KCl mixtures with 2 mol % K_2TiF_6 [23].

Figure 9 shows the SEM photographs of titanium deposits with pulse current at 823 K. The surface morphology changes with electrodeposition time, i.e., the bigger grains are generated with continuous electrodeposition. From the SEM photograph of the cross-section (for 3.6 ks), it is observed that finer grains formed during the initial electrodeposition remained

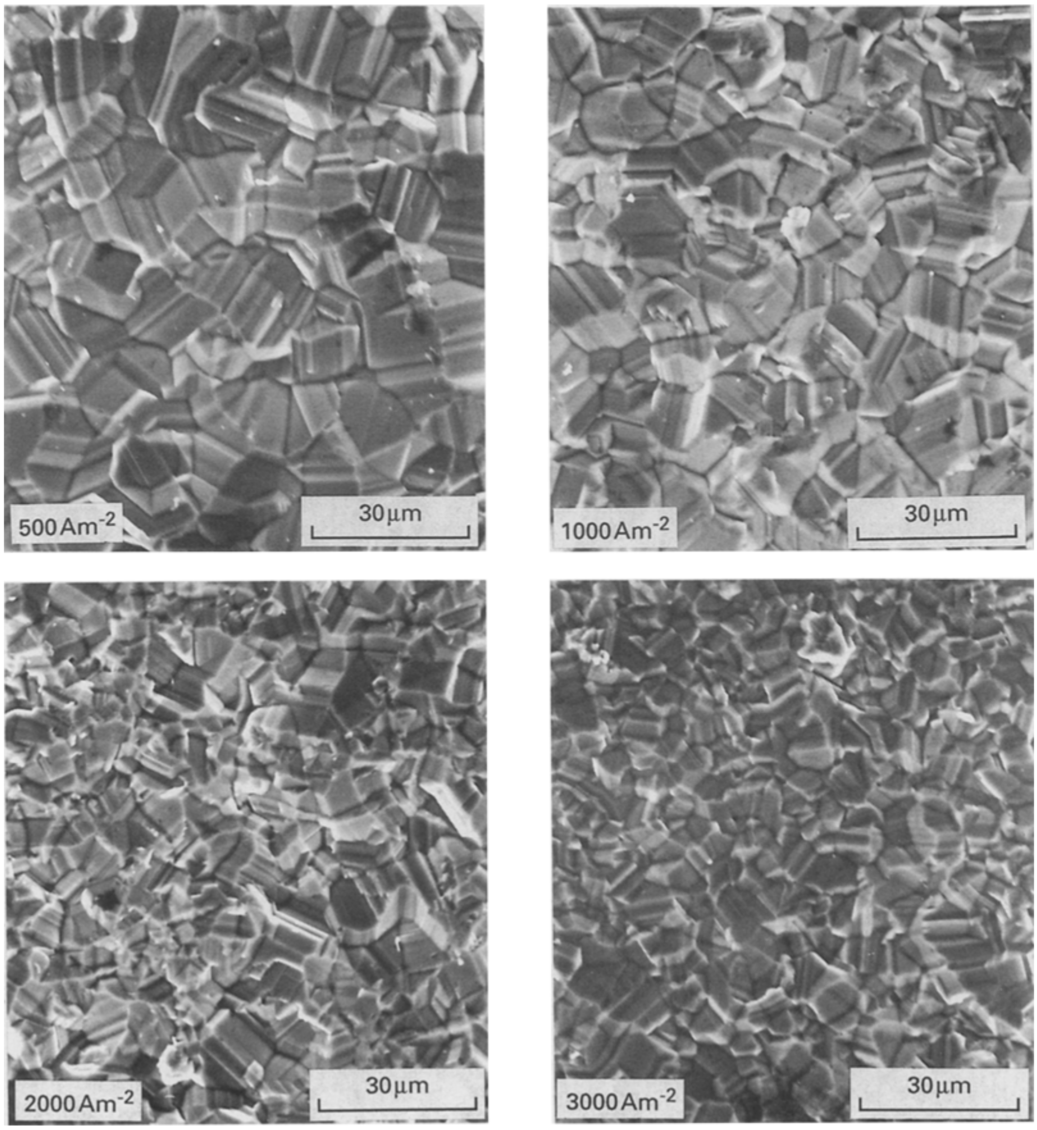

Fig. 11. SEM micrographs of the surface of titanium deposits at 873 K for 3.6 ks at different I_2 of the pulse current in KCl–NaCl–LiCl + 2 mol % K_2TiF_6.

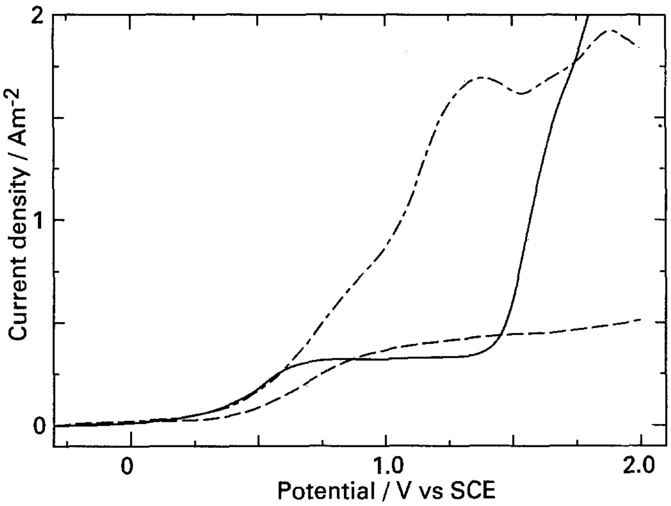

Fig. 12. Polarization curves of titanium deposits in 3% NaCl solution at 298 K, which were prepared for 3.6 ks at 923 K in KCl–NaCl–LiCl + 2 mol % K_2TiF_6. Curves: (——) pure Ti sheet, (– – –) Ti deposits with pulse current and (- - - -) Ti deposits with constant current.

up to a certain thickness inside the deposits, and some of the grains grew with time. Although steel and titanium differ in their thermal expansion coefficients, the deposits did not exhibit fissures and cracks. This is possibly due to generation of a very thin layer of a gradient Ti–Ni alloy.

3.3. *Effect of current density*

In the case of pulse current electrolysis for 720 C cm^{-2} at 873 K, the influence of the current density (I_2) on the preferred orientation and the morphology of the deposits was investigated. Figure 10 shows the change of the orientation index for titanium deposits with variation of current density. It was found that the (1 1 0) face was preferred in this experiment. The remarkable orientation to (1 1 0) was, in particular, obtained at a current density of 1000 A m^{-2}. Titanium deposits exhibit random textures at low current density of 500 A m^{-2} and high current density of 3000 A m^{-2}; it is considered that the growth at low and high rates is not pertinent to the generation of deposits with preferred orientation.

SEM photographs for the deposits are shown in Fig. 11. It can be seen that the morphology of the deposits was a function of the current density (I_2). The deposits at each current density had a granular structure. Grains became increasingly small with increasing current density (I_2), due to the formation of a greater number of nuclei.

3.4. *Corrosion resistance*

From the polarization curves in 3% NaCl solution shown in Fig. 12, the corrosion resistance of the deposits obtained by pulse current was better than that by constant current, and no pitting corrosion occurred even at higher potential than 1.5 V vs SCE. It was also obvious that the passivation potential range of the deposit by pulse current was wider. This implies that the deposits by pulse current have a better quality than those by constant current. It is possible that the deposits obtained by pulse current above 873 K can be used as real pure titanium coatings and as anticorrosive coatings.

4. Conclusions

Under constant and pulse current electrolysis titanium films were electrodeposited at various temperatures, current densities and electrolysis times from molten chloride–fluoride mixture. The crystal orientation and morphology of the deposits were found to change with the conditions. The results may be summarized as follows:

(i) With increase in temperature, the crystal orientation of titanium deposits changed to (0 0 2) under constant current and to (1 1 0) under pulse current. The grain size of deposits having granular structure became bigger with increasing temperature.

(ii) The preferred orientation and morphology of the deposits changed as the electrodeposition time and current density, I_2, increased.

(iii) Titanium deposits above 873 K with pulse current had a better corrosion resistance than pure titanium sheet.

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