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Pulse electrodeposition of titanium on carbon steel in the LiF–NaF–KF eutectic melt

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Abstract

Electrodeposition of titanium was carried out in the K_3TiF_6–LiF–NaF–KF melt using both direct (DC) and unipolar pulse current (PC) techniques. Dense and smooth titanium coatings were obtained by PC plating at 750 °C whereas DC plating led to rough and dendritic deposits. The best results were obtained using a 100 μC cm^{-2} pulse charge and a cathodic current density of 50 and 75 mA cm^{-2}. The cathodic current efficiency was in the range 60–65%. The titanium deposits obtained under such conditions behaved similarly to CP-titanium in NaCl and HNO_3 solutions at room temperature.

1. Introduction

The electrodeposition of titanium is a useful method for corrosion protection in sea-water and chemical environments.

Many attempts have been made to obtain titanium electrodeposits from organic [1, 2], aqueous [3, 4] and molten salt media [5–18], but pure titanium was only obtained from the latter, especially in chloride [5–8], fluoride [9–14] and mixed chloride–fluoride melts [15–18]. Chloride melts generally led to powdery [6] or dendritic [7, 8] deposits due to the existence of three low-stability titanium oxidation states and disproportionation reactions. In fluoride melts, only two oxidation states exist and the high stability of the titanium fluoride complexes results in two reduction steps [13, 14]:

$$TiF_6^{2-} + e^- \rightarrow TiF_6^{3-}$$
$$TiF_6^{3-} + 3\,e^- \rightarrow Ti + 6\,F^-$$

Compact and uniform deposits of pure titanium were obtained from NaF–K_2TiF_6 at 950–1000 °C [9, 10] and LiF–NaF–KF–K_2TiF_6 at 700 °C [11, 13, 14] and 800 °C [12] by direct current electrolysis. Nevertheless, these coatings became rougher, and sometimes dendritic, as the cathodic current density and/or the deposition time increased. In mixed chloride–fluoride melts, pure and compact titanium coatings [15, 17] as well as powdery and dendritic deposits [18] can be obtained, depending on the $[F^-]/[Cl^-]$ ratio.

Depending on the metallic substrate and the temperature, intermetallic compounds can be formed under the external pure titanium layer during electrolysis in fused salts. Such behaviour was observed on copper [13], nickel [14] and iron [19, 20].

Pulse plating of zinc, cadmium, nickel, chromium and precious metals in aqueous media [21] and molybdenum [22], chromium [23], tungsten [24], niobium [25] and titanium [17] in fused salts, improves the properties of the deposits. Dense, not dendritic coatings can be obtained because concentration polarization is minimized by use of pulse current. In this paper we present our results on electrocoating of titanium on carbon steel in the LiF–NaF–KF eutectic melt using this technique. The cathodic current efficiencies, morphologies and microhardnesses of the deposits obtained by direct and pulse current are compared. The electrochemical behaviour of the electrocoatings is evaluated in NaCl and HNO_3 solutions at room temperature.

2. Experimental details

The LiF–NaF–KF eutectic (46.5–11.5–42 mol %) (MP = 454 °C) was prepared by mixing finely crushed fluorides (P.A.) in a glove box under dry argon, placing them in a nickel crucible and introducing it in the electrolysis cell. The mixture was maintained under vacuum (nearly 3×10^{-5} atm) and heated by 100 °C steps to 300 °C for dehydration and then melted at 600 °C under pure argon atmosphere. After cooling, the titanium salt, K_2TiF_6 (P.A.), was introduced to the crucible and the same procedure was repeated. After melting, the tetravalent titanium ions were reduced to the trivalent state by connecting the crucible to a titanium rod immersed in the bath, according to the following reaction:

$$3\,\mathrm{TiF}_6^{2-} + \mathrm{Ti} + 6\,\mathrm{F}^- \rightarrow 4\,\mathrm{TiF}_6^{3-}$$

The moisture and metallic impurities of the melt were eliminated by a 48 h preelectrolysis at 700 °C using both titanium anode and cathode and 15 mA cm^{-2} cathodic current density.

For the electrodeposition study, commercially pure titanium bars (ASTM grade 3) (10 mm × 10 mm × 110 mm) and AISI 1020 carbon steel sheets or rods (1 mm × 15 mm × 90 mm and dia. 10 mm) were used. Their chemical compositions are presented in Table 1.

The titanium anodes were previously etched in a HF–HNO_3 (20–80 v/v) solution, and the steel cathodes were electropolished in a $HClO_4$–CH_3CH_2OH–glycerine (20–70–10 v/v) solution [26], then rinsed with distilled water and dried with acetone.

During the electrodeposition experiments, four anodes were used, symetrically arranged around the cathode.

The experiments were carried out between 700 and 900 °C by means of direct current (DC) and at 750 °C by means of unipolar pulse current (PC).

After all the experiments, the cathodes were lifted above the bath level for draining, removed from the cell, washed in distilled water submitted to ultrasounds in order to remove the solidified bath which could be retained on the deposits or between the dendrites, dried with acetone and weighted. The cathodic current efficiency was calculated from the mass gain. The microhardness of the deposits was measured from cross-sections of the cathodes. The microstructure was analysed by X-ray diffraction and the morphology was evaluated by means of optical and scanning electron microscopy. The chemical composition was determined in an inductively coupled plasma spectrophotometer and gas analyses were carried out by means of the technique of sample melting and inert carrier gas. Potential–current curves of 1020 steel, CP-titanium and PC titanium electrocoatings were obtained in 3 wt % NaCl and 30 wt % HNO_3 solutions at room temperature, after stabilization of the open-circuit potential.

3. Results and discussion

3.1. *DC titanium electrodeposition*

DC electrodeposition was performed on steel rods in the 700–900 °C temperature range for 18–60 mA cm^{-2} cathodic current density for 1 h. The cathodic current efficiencies measured for electrolysis performed in a 2.2 wt % Ti(III) solution are presented in Table 2. The highest efficiencies (between 62 and 85%) were obtained at 750 °C. At 800 °C, the highest efficiency (55%) was measured for very low current density. At 900 °C, the efficiency was always below 30%. These low current efficiencies measured at the highest temperatures can be explained by the higher contribution of K^+ reduction to the total current, as shown in a previous paper [27]. The presence of large amounts of condensed potassium on the internal walls of the electrolysis cell confirmed this hypothesis. At 750 °C, the coatings were continuous but rougher and more dendritic than those obtained at 700 °C.

Table 1. Chemical composition of 1020 carbon steel cathodes and CP-titanium anodes (in wt ppm except when noted)

1020 carbon steel									
Fe	C	Mn	P	S					
bal.	1700–2300	3000–6000	400	500					
CP-titanium									
Ti/wt %	Fe	Cu	Ca	Mg	Si	O	N	S	C
99.3	168	6	40	10	20	2700	110	150	100

Table 2. Cathodic current efficiency against temperature and cathodic current density for titanium electrodeposition on steel rods in a 2.2 wt % Ti(III) solution

Temperature /°C	Cathodic current density /mA cm^{-2}	Cathodic current efficiency /%
700	35	59
750	18	70
	35	85
	48	72
	60	62
800	18	55
	48	29
	60	35

Cross-sections of deposits show a single layer of pure titanium for electrolysis performed at 700–750 °C and three layers for experiments performed at 800–900 °C (Figures 1 and 2). Electron probe microanalysis revealed that they are composed of the intermetallic compounds Fe_2Ti (near the steel substrate) and FeTi (intermediate layer) and pure titanium (external layer). A Kirkendall region near the Fe_2Ti/steel interface which formed due to the higher diffusion rate of iron in titanium than the other way is clearly noted on the titanium deposit obtained at 900 °C. This area of defects is prejudicial to

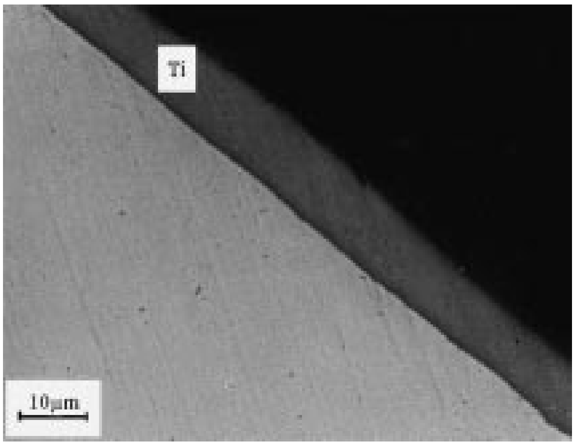

Fig. 1. SEM photograph of the cross-section of a titanium deposit obtained at 700 °C using a 35 mA cm^{-2} DC density.

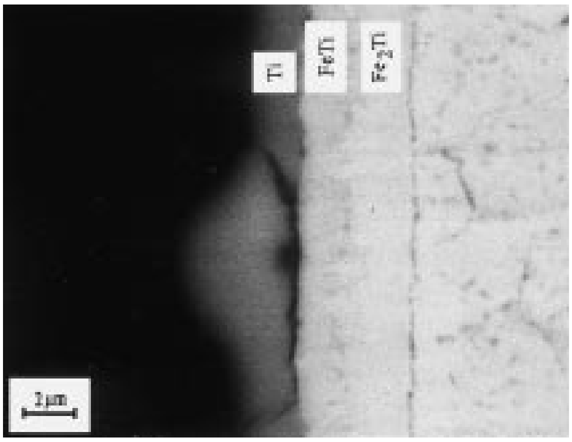

Fig. 2. SEM photograph of the cross-section of a titanium deposit obtained at 900 °C using a 260 mA cm^{-2} DC density.

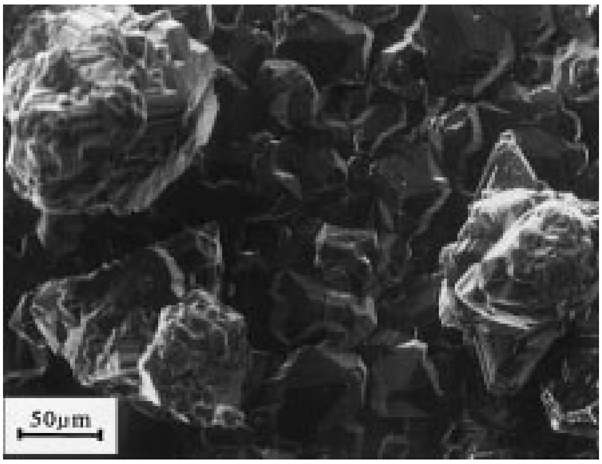

Fig. 3. SEM photograph of a titanium deposit obtained at 750 °C using a 35 mA cm^{-2} DC density.

the adherence of the coating. The presence of cracks in the titanium layer for the coatings obtained at 900 °C (Figure 2) may be due to the b.c.c. to h.c.p. phase transition of titanium at 882 °C [28] during cooling.

DC electrodeposition on steel sheets at 750 °C showed lower current efficiencies than for steel rods (Table 3). Moreover, the deposits presented many dendrites on the surface and at the edges of the cathodes where the current is expected to have higher density. Figure 3 shows the morphology of a coating obtained at 750 °C during DC plating, where dendrites developed perpendicularly to the surface. Figure 4 presents a cross-section of this deposit. The lower cathodic current efficiencies can be attributed to the loss of the finest dendrites during electrolysis and posterior cleaning.

3.2. *Unipolar PC titanium electrodeposition*

The unipolar PC plating consists in applying periodically a J_p cathodic current density during T_{on} and switching off the power during T_{off}. Two main methods are generally used:

(i) varying J_p with constant T_{on} and $J_m\left(=\frac{T_{on}J_p}{T_{on}+T_{off}}\right)$

(ii) varying J_p with constant $J_m(T_{on}+T_{off})$

In the first method, an increase in J_p leads to an increase in T_{off}. Since both J_p and T_{off} influence crystallization [21], it is not clear whether the grain size results from J_p or T_{off} changes. We preferred the second technique where T_{off} does not vary much.

We chose to carry out the unipolar PC experiments in 2.2 wt % Ti(III) solutions for 3 h using the electrolysis parameters which gave the best results in DC plating: a 750 °C temperature and a J_m average cathodic current of 35 mA cm^{-2}. The electrodeposition was made on steel sheets where PC plating was expected to have more influence on the morphology of the coatings. The values of $J_m(T_{on}+T_{off}) = J_pT_{on}$ pulse charge density and J_p pulse current density were in the 10–100 μC cm^{-2} and 50–150 mA cm^{-2} ranges, respectively.

Table 3. Cathodic current efficiency against cathodic current density for titanium electrodeposition on steel sheets in a 2.2 wt % Ti(III) solution at 750 °C

Cathodic current density /mA cm^{-2}	Cathodic current efficiency /%
35	43
45	24
55	29

The cathodic current efficiencies and the morphologies of the deposits obtained by PC plating are reported in Table 4. For low pulse charge (10 μC cm^{-2}), the coatings are composed of a very thin compact titanium layer covered by numerous fine dendrites. The large fluctuation in the current efficiency is probably due to the loss of dendrites during electrolysis and cleaning. For higher pulse charges (50 and 100 μC cm^{-2}), the coatings, 50 to 100 μm thick, are smooth and adherent (Figure 5) and dendrites sometimes present were principally localized at the edges of the cathodes. The cathodic current efficiency is higher for 100 μC cm^{-2} than for 50 μC cm^{-2} pulse charge and seems not to depend significantly on the J_p pulse current density for

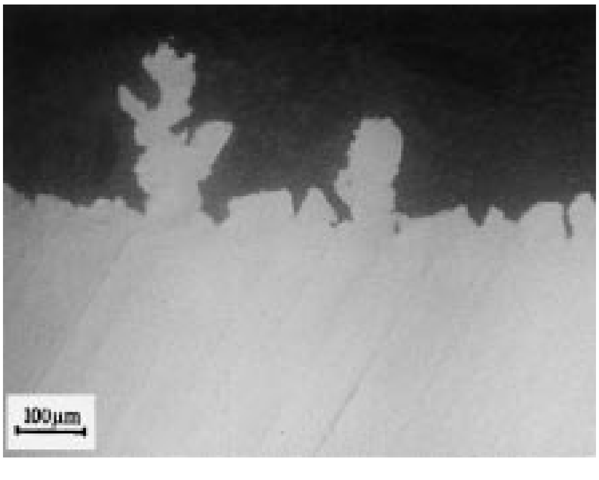

Fig. 4. Optical photograph of the cross-section of a titanium deposit obtained at 750 °C using a 35 mA cm^{-2} DC density.

Table 4. Cathodic current efficiency and morphology of the titanium deposits against unipolar PC plating parameters (T = 750 °C; t = 3 h; J_m = 35 mA cm^{-2})

J_mT /μC cm^{-2}	J_p /mA cm^{-2}	T_{on} /ms	T_{off} /ms	Cathodic current efficiency /%	Morphology of the deposit
10	100	0.10	0.18	33	very dendritic
10	75	0.13	0.15	75	very dendritic
10	50	0.20	0.08	45	dendritic
50	100	0.50	0.91	52	smooth with defects
50	75	0.67	0.74	48	smooth with dendrites at the edges
50	50	1.00	0.41	60	smooth with dendrites at the edges
100	150	0.67	2.10	63	smooth with dendrites at the edges
100	100	1.00	1.80	70	smooth with dendrites at the edges
100	75	1.33	1.50	65	very smooth
100	50	2.00	0.80	58	very smooth

the same pulse charge. The current efficiencies measured for PC plating are higher than the values obtained for DC plating (Table 3).

It is known that during PC plating, the continuous charge and discharge of the double layer may influence the metal deposition, especially when T_{on} and T_{off} are lower or of the same order than t_c charge and t_d discharge times. In such conditions, the cathodic current is strongly damped and the advantages of PC plating can be lost. This approach of PC plating to DC plating can be evaluated from the degree of flattening of the J_F faradic current:

$$\Delta = \frac{J_p T_{on} - \int_0^{T_{on}} J_F \, dt}{J_m T_{off}} \tag{1}$$

Δ increases from 0.1 to 0.9 when T_{on} varies from 10 t_c to 0.1 t_c [21].

An estimation of t_c as a function of J_p can be obtained from the relation [21]:

$$t_c = \frac{4RTC}{\alpha n F J_p} \tag{2}$$

Fig. 5. Optical photograph of the cross-section of a titanium deposit obtained at 750 °C using a 50 μC cm^{-2} pulse charge and a 50 mA cm^{-2} PC density.

where T is the temperature (in K), α is the charge transfert coefficient, n is the exchanged electron number, and C is the double layer capacity (in μF cm^{-2}).

Using T = 1023 K, n = 3 and considering the usual values of α and C, 0.5 and 50 μF cm^{-2} respectively, we calculated the approximated t_c values for J_p ranging from 50 to 150 mA cm^{-2} (Table 5). The values of the degree of flattening were approximated from the $\Delta = f(T_{on}/t_c)$ curve proposed by Puippe [21] and are reported in Table 6. For experiments made with 10 μC cm^{-2} pulse charge, T_{on}/t_c is lower than 1 and a high degree of flattening is calculated (from 0.43 to 0.61). This can explain why the morphology of the deposits appeared dendritic like the coatings obtained by DC plating. On the other hand, for 50 and 100 μC cm^{-2} pulse charges, as the Δ degree is lower (nearly 0.1), the charge of the double layer is expected to have less influence. This seems to be confirmed as PC plating in these conditions yields better titanium coatings than those obtained by DC plating.

Figure 6 shows the surface morphology of coatings obtained with 50 mA cm^{-2} pulse current density and 50 μC cm^{-2} pulse charge. For the same pulse current, no influence of the pulse charge on the grain size is noted. A slight decrease in the grain size can be observed when the pulse current density increases. All deposits present well-crystallized grains whose size was between 50 and 100 μm. In all cases, the titanium grain size for PC

Table 5. Approximated t_c charge time of the double layer as a function of J_p pulse current density obtained from Relation 2

J_p/mA cm^{-2}	50	75	100	150
t_c /ms	0.235	0.156	0.117	0.078

Table 6. Δ degree of flattening for the PC experiments presented in Table 4

J_m (T_{on} + T_{off})/μC cm^{-2}	T_{on}/t_c	Δ
10	0.85	0.43–0.61
50	4.25	0.10–0.16
100	8.50	0.04–0.09

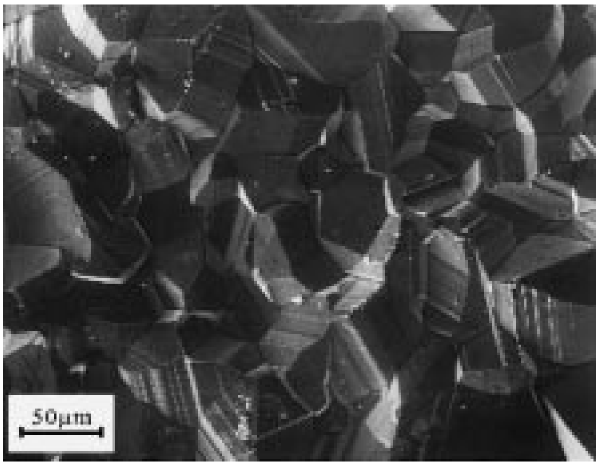

Fig. 6. SEM photograph of a titanium deposit obtained at 750 °C using a 50 μC cm^{-2} pulse charge and a 50 mA cm^{-2} PC density.

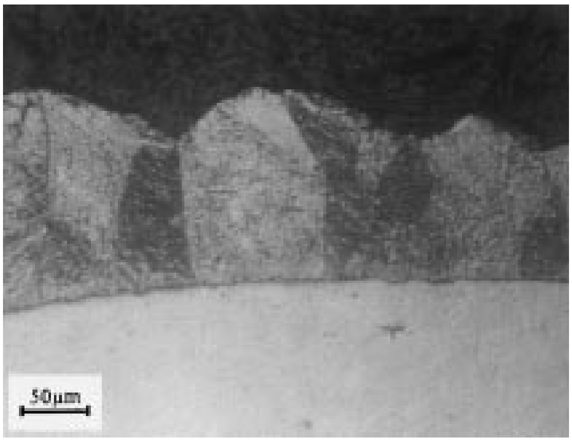

Fig. 7. Optical photograph of the cross-section of a titanium deposit obtained at 750 °C using a 100 μC cm^{-2} pulse charge and a 100 mA cm^{-2} PC density after etching in a 5 wt % HF solution during 60 s.

plating (Figure 6) is higher than the grain size for DC plating, from 25 to 50 μm (Figure 3).

The cross-sections of the coatings, etched in a 5 wt % HF solution for 60 s, depict the characteristic columnar structure of refractory metal deposits obtained by electrolysis in molten salts (Figure 7).

No influence of the PC plating parameters on the microhardness of the titanium deposit was observed. The average microhardness, measured at the middle of the deposit cross-sections with a 25 g load during 15 s, is in the HV 130 ± 30 range. This value is lower than those obtained for DC coatings (HV 240 ± 40) and for CP-titanium anodes (HV 223 ± 5) which had smaller grains. We noted that the microhardness of the deposits decreases from the steel/titanium interface to the titanium surface, indicating coarsening of the grains.

X-ray diffraction patterns of the PC titanium electrodeposits obtained at 100 μC cm^{-2} pulse charge only show the (0 0 2), (0 1 1) and (0 1 2) peaks (Figure 8). The orientation indexes calculated from the relation:

$$\text{Orientation index} = \frac{I_{hkl}/\sum I_{hkl}}{I_{\text{ASTM}\,hkl}/\sum I_{\text{ASTM}\,hkl}}$$

where I_{hkl} and $I_{\text{ASTM}\,hkl}$ are the integrated intensities from an (hkl) peak, obtained for the deposits and for titanium of random texture [29] respectively, are shown in Figure 9. At low current density, the titanium deposits exhibit a random texture. For 100 mA cm^{-2}, the coatings show (0 1 2) and (0 0 2) preferred orientations and for 150 mA cm^{-2}, the (0 1 2) face is preferred.

Chemical analysis of the titanium coatings obtained at 750 °C shows a lower iron content (3–18 wt ppm) than the original iron concentration of the anodes (168 wt ppm), which supports the efficiency of the

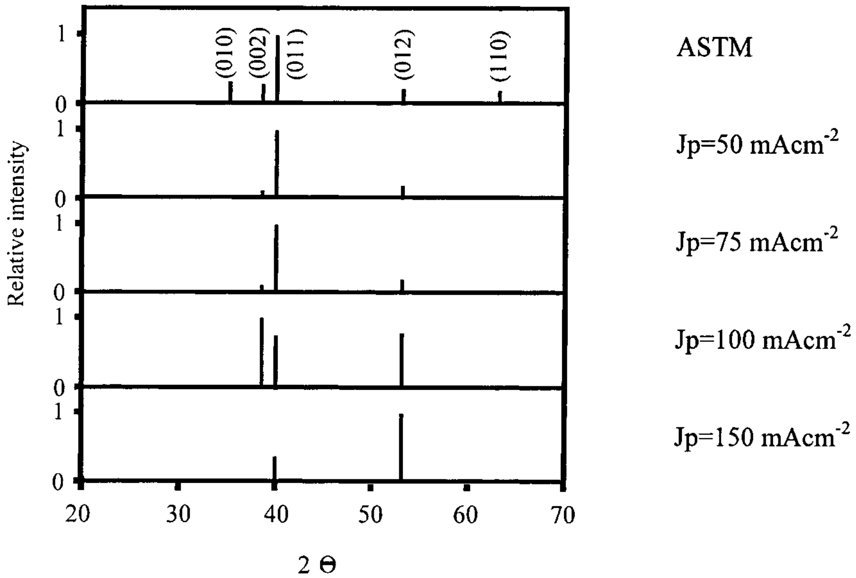

Fig. 8. X-ray diffraction patterns of titanium deposits obtained at 750 °C using a 100 μC cm^{-2} pulse charge and different PC densities.

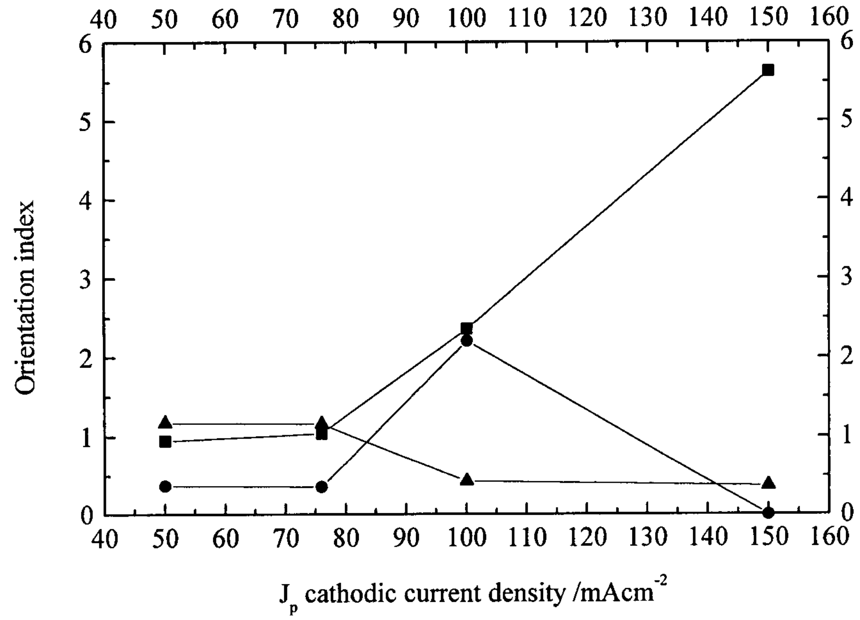

Fig. 9. Influence of PC density on the orientation index of titanium deposits obtained at 750 °C using a 100 μC cm^{-2} pulse charge. Key: ●—● (0 0 2); ▲—▲ (0 1 1); ■—■ (0 1 2).

electrolysis for titanium refining. It is well known that the presence of iron in titanium, even at low levels, reduces the corrosion resistance significantly [30]. The oxygen content in the electrodeposits (1350 wt ppm) is lower than in the anodes (2700 wt ppm).

Polarization curves of 1020 steel, CP-titanium and PC titanium electrocoatings in 3 wt % NaCl and 30 wt % HNO_3 solutions at room temperature are presented in Figures 10 and 11. We note that titanium deposits obtained with 50 and 100 μC cm^{-2} pulse charges (electrocoatings 1 and 2) behaved similarly to CP-titanium in NaCl and HNO_3 solutions. Microscopic observations of the coating surfaces revealed no localized corrosion. These results show that PC titanium electrodeposits obtained under such conditions could be used as anticorrosive coatings. On the other hand, the high anodic current densities measured for the deposits obtained with 10 μC cm^{-2} (electrocoating 3) in NaCl solutions suggest corrosion of the substrate. Several points of attack were noted and certainly originated from existing defects in the deposits. Indeed, cleaning of dendritic deposits after electrodeposition usually led to the breaking of dendrites and sometimes to the simultaneous removal of adjacent coating (Figure 12). Such deposits do not provide corrosion protection to the substrate.

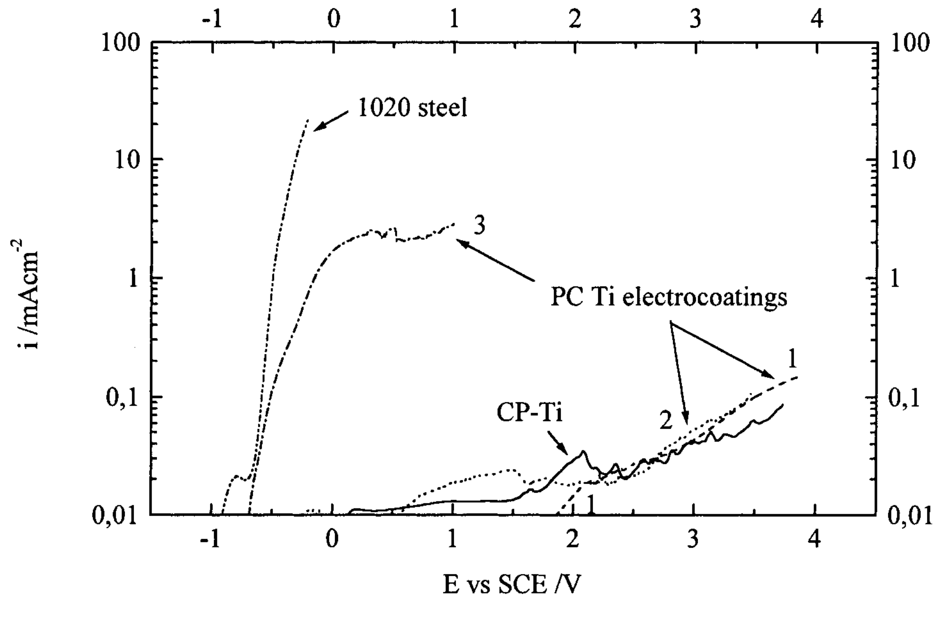

Fig. 10. Anodic polarization curves of 1020 carbon steel, CP-titanium and titanium deposits (obtained at 750 °C by PC plating using: (1) 50, (2) 100 and (3) 10 μC cm^{-2}) in 3 wt % NaCl solution at 25 °C using a 2 mV s^{-1} scan rate.

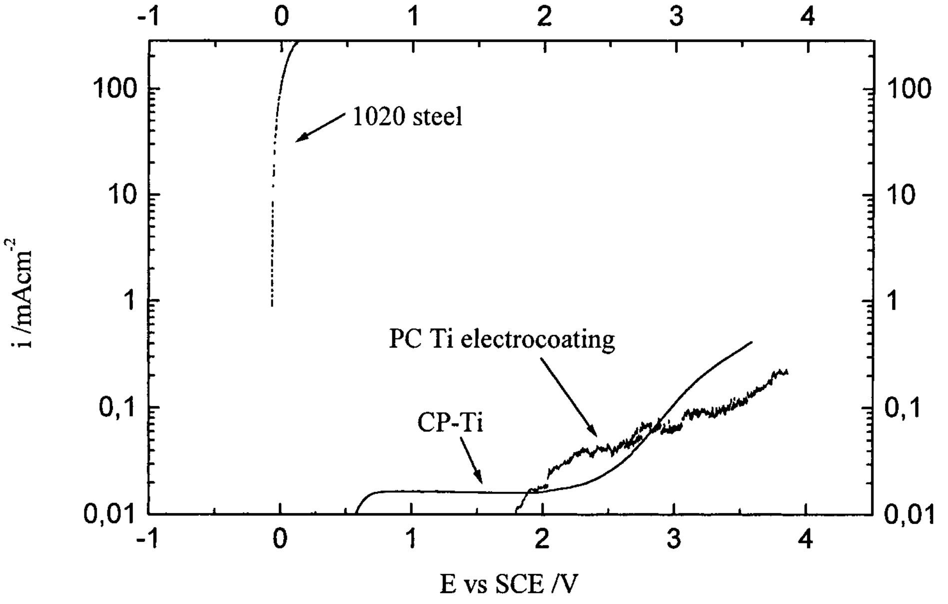

Fig. 11. Anodic polarization curves of 1020 carbon steel, CP-titanium and titanium deposit (obtained at 750 °C by PC plating using 50 μC cm^{-2}) in 30 wt % HNO_3 solution at 25 °C using a 2 mV s^{-1} scan rate.

4. Conclusions

Electrodeposition of titanium on carbon steel was performed by direct and unipolar pulse current electrolysis in the LiF–NaF–KF eutectic melt. Under DC plating, the best efficiencies, around 80–85%, were obtained at 750 °C with a 35 mA cm^{-2} cathodic current density, but the deposits, consisting of a single layer of pure titanium, were dendritic. At higher temperatures, the efficiencies were lower ($<55\%$) and the coatings presented intermediate layers of FeTi and Fe_2Ti intermetallic compounds and a region of Kirkendall defects which were detrimental to the adherence of the deposits. Unipolar PC plating carried out at 750 °C, using a 35 mA cm^{-2} average current density, improved the morphology of the deposits. Dense, smooth and adherent titanium coatings consisting of well-crystallized, joined grains were obtained with efficiencies in the 50–70% range, using 50 and 100 μC cm^{-2} pulse charges and 50 to 100 mA cm^{-2} pulse current densities. These deposits presented lower iron and oxygen contents and lower microhardness than the CP-titanium anodes. Their corrosion resistance, evaluated from potential-current curves obtained in 3 wt % NaCl and 30 wt % HNO_3 solutions at room temperature, is similar to that of CP-titanium. Lower pulse charges (10 μC cm^{-2}) led to dendritic deposits, comparable to those obtained by DC plating. The reason is probably the damping of the faradic current due to the double layer charging at low cathodic pulse times.

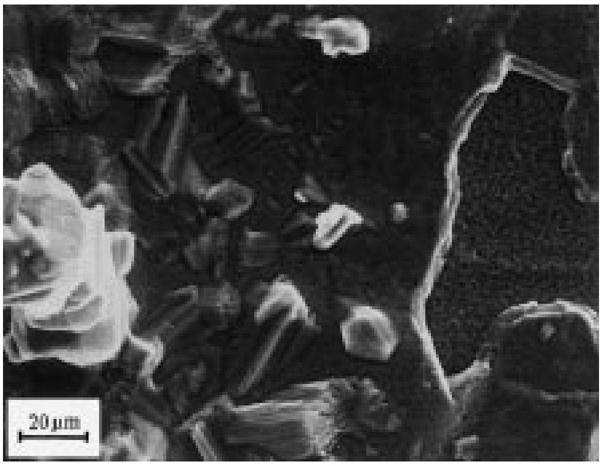

Fig. 12. SEM photograph of a titanium deposit showing a superficial defect caused by the breaking of a dendrite during ultrasonic cleaning.

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