

CHARACTERIZATION OF DSA-TYPE OXYGEN EVOLVING ELECTRODES. CHOICE OF BASE METAL

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ABSTRACT

In the search for a good DSA-type O₂-evolving electrode, the influence of the base metal (titanium, tantalum, zirconium, niobium and some of their alloys) on the performance of IrO₂-Ta₂O₅ coated electrodes, was investigated. The thermal behaviour and oxygen affinity sequence of the metals, in relation to the electrode preparation procedure, were determined thermogravimetrically. The chemical and electrochemical stability of the base metal was found to be directly related, through the wear mechanism, to the service life of the electrode, measured in 30% H₂SO₄ at 80 °C and 750 mA cm⁻².

Tantalum-based electrodes were shown to have the highest service life; 1700 h, compared with the 120 h for titanium-based electrodes.

INTRODUCTION

During the past ten years, the electrochemical properties of titanium anodes coated with a layer of RuO₂ and TiO₂, so-called dimensionally stable anodes-type chlorine (DSA-Cl₂) electrodes, have been extensively studied and have satisfactorily solved the problems associated with the electrochemical production of chlorine and caustic soda [1–3].

The situation is very different for DSA-type oxygen-evolving electrodes (DSA-O₂) which are operated in corrosive electrolytes at high current densities. The main problem here is the rapid loss of activity, generally manifested by an increase in potential after a certain operating time. One of the reasons for such an activity loss is the poor performance of the base metal used. In the patent literature [4,5] all the valve metals (titanium,

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zirconium, niobium and tantalum) and their alloys have been proposed as base metals, but there is no information on the influence of base metal on the service life.

In this paper the influence of the base metal on the service life of the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coating [6,7] is investigated.

EXPERIMENTAL

Electrode preparation

The test electrodes were prepared by the thermal decomposition technique [8] in air, or in argon saturated with water. To ensure maximum adhesion of the coating, the base metal (see Table 1 for the characteristics of the base metals used) was sand-blasted, etched in appropriate corrosive media, then washed with water and finally dried in air.

$\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and TaCl_5 were dissolved in an ethanol-isopropanol mixture in the amounts required to form an IrO_2 (70 mol %)- Ta_2O_5 (30

TABLE 1
Characteristics of the base metals used

Base metal	Ti	Zr	Nb	Ta	Nb-1% Zr	Ta-40% Nb
ASTM code	B256	R60702	R0412	R0200	R04261	—
Atomic mass	47.88	91.22	92.90	180.94	—	—
Density (g cm^{-3})	4.5	6.5	8.6	16.6	8.6	13.4
Melting point ($^{\circ}\text{C}$)	1800	1852	2468	2996	—	—
Resistivity ($\mu\Omega \text{ cm}$)	54	44	16	13.5	—	—
Compo- sition (wt.%)	Al	0.009				
	C	0.01				
	Cr		0.016			
	Cu		0.002			
	Fe	0.05	0.08	0.002	0.002	0.002
	Hf		4.5	0.003	0.003	
	Mo		0.002	0.002	0.002	0.002
	Nb			balance	balance	40 ± 4
	Ni		0.002	0.002	0.002	0.003
	Pb		0.002			
	Si		0.01	0.002	0.002	0.002
	Sn		0.002			
	Ta			0.065	0.065	balance
	Ti	balance	0.002	0.001		0.001
	W		0.01	0.01	0.01	0.01
	V		0.002			
	Zr		95.34	0.003		1 ± 0.1

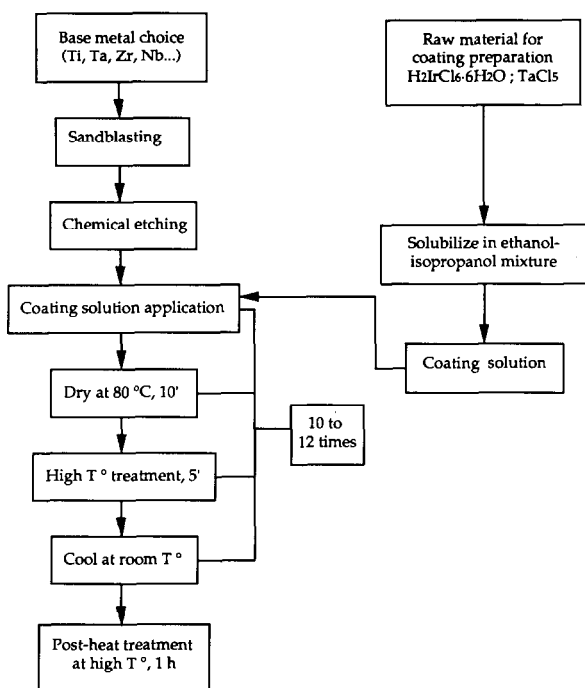


Fig. 1. Method of preparation of the DSA-O₂ anodes.

mol%) coating. This solution was applied by brush on the pretreated base metal in twelve sequential coatings. After each coating, the sample was dried at 80 °C then placed in a preheated furnace for 5 min at a predetermined temperature. The final coating was heated at the fixed temperature for 1 h (Fig. 1). The amount of material deposited on the base metal was $40 \pm 5 \text{ g m}^{-2}$.

Thermogravimetric measurements

Thermogravimetric measurements were done on a Mettler 197 electromagnetically-compensated thermobalance. Samples of each base metal were heated in air and the changes in weight were recorded as a function of time for a fixed temperature, or as a function of temperature for a linear increase of temperature with time ($2^\circ \text{C min}^{-1}$).

Anodic stability of base metals

The anodic stability of the base metals was investigated under potentiostatic conditions by anodic polarization at 2 V ($\text{Hg}/\text{Hg}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ satd.) and by measuring the weight loss of the samples at different H_2SO_4 concentrations.

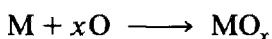
Service life test

To measure its service life τ , the electrode is polarized anodically in 30% H_2SO_4 at 80°C under galvanostatic conditions (750 mA cm^{-2}) and the anode potential recorded as a function of time. The τ value for a given electrode is the time at which the anode potential increases significantly (about 5 V); at this stage the electrode is said to have lost its activity. At least five electrodes were used for each experiment.

RESULTS AND DISCUSSION

Thermal stability of the base metal

During the preparation of the coating on the base metal, the sample is heated at high temperature ($500\text{--}550^\circ\text{C}$) in presence of oxygen, so as to cause thermal decomposition of H_2IrCl_6 and TaCl_5 to IrO_2 and Ta_2O_5 respectively. Under these conditions, surface oxidation of the base metal (M) also occurs with the formation of an oxide (MO_x)



This build up of an oxide layer between the coating and the base metal can have deleterious effects, such as exfoliation of the coating or formation of an insulating layer between the base metal and the coating.

The growth of an oxide film on a metal surface during heat treatment at constant temperature can be described by five different kinetic laws [9]

$$\text{linear} \quad \Delta m = Kt \quad (1)$$

$$\text{parabolic} \quad (\Delta m)^2 = Kt \quad (2)$$

$$\text{cubic} \quad (\Delta m)^3 = Kt \quad (3)$$

$$\text{logarithmic (direct)} \quad \Delta m = Kt(\log At + 1) \quad (4)$$

$$\text{logarithmic (reverse)} \quad \Delta m = \frac{K}{A - \log t} \quad (5)$$

where Δm is the weight increase per unit of surface; t is the time; and A , K are the constants.

To study the kinetics of oxide formation from the valve metals, thermogravimetric measurements were carried out in air at six different temperatures. Figure 2 shows typical thermogravimetric curves (increase of weight as a function of time) obtained for the valve metals tested.

By fitting the experimental curves with the five laws, the correlation coefficients can be calculated (Table 2). This table clearly shows that the

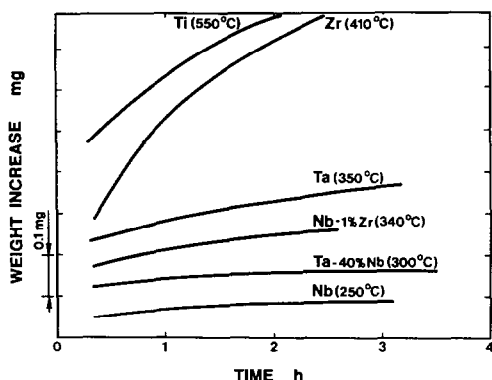


Fig. 2. Thermogravimetric curves of base metals obtained in air at different fixed temperatures.

kinetics of oxide formation on a valve metal surface follow the parabolic law (eqn. 2). From these values the activation energies for M_{ox} have been calculated using the Arrhenius relation.

$$k = A e^{-E/RT}$$

where E is the activation energy; k is the rate constant for a given temperature and O_2 concentration; T is the absolute temperature; R is the gas constant; and A is the pre-exponential factor (constant). The Arrhenius plot, $\ln k = f(1/T)$, for the different valve metals is shown in Fig. 3, and the activation energies calculated from the slopes of the straight lines are given in Table 3. These values are in good agreement with those given in the literature for slightly different oxidation conditions [10].

The discontinuities and changes in slope observed in Fig. 3 can be attributed to changes in the expansion coefficients Δ defined as

$$\Delta = \frac{M_{\text{ox}}}{\rho_{\text{ox}}} \frac{\rho_m}{M_m}$$

TABLE 2

Correlation coefficients obtained by fitting the experimental curves of Fig. 2 with the five kinetic laws given in the text

Metal	Temperature (°C)	Correlation coefficients for eqns.				
		(1)	(2)	(3)	(4)	(5)
Ti	550	0.924	0.995	0.971	0.999	0.982
Zr	410	0.958	0.993	0.977	0.999	0.987
Nb	250	0.943	0.984	0.967	0.991	0.981
Ta	350	0.951	0.898	0.991	0.994	0.934
Nb-1% Zr	340	0.953	0.973	0.978	0.999	0.931
Ta-40% Nb	300	0.970	0.958	0.983	0.985	0.942

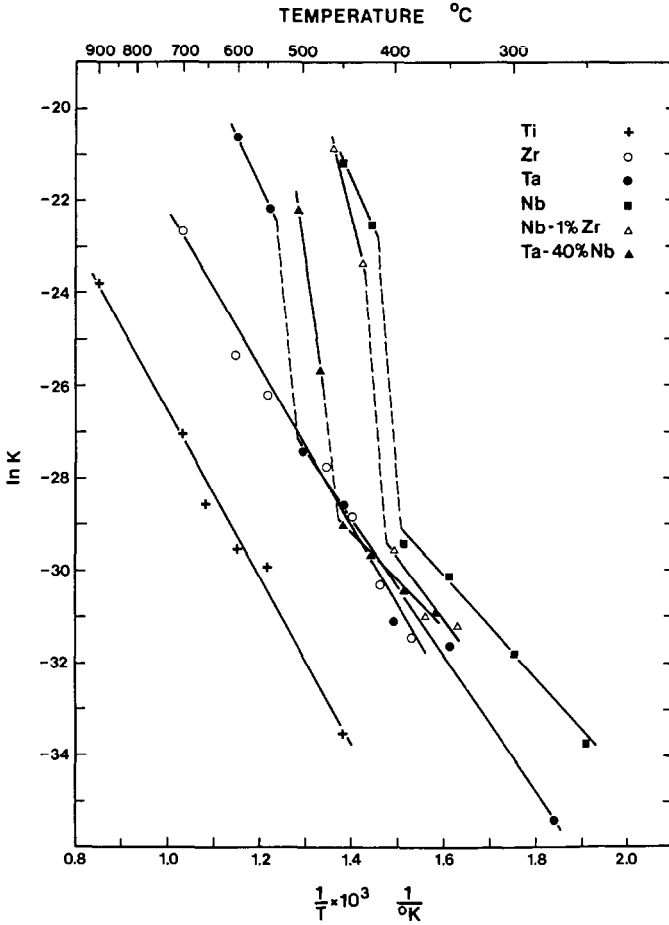


Fig. 3. Arrhenius plot for the oxidation of base metals in air.

where $M_{\text{ox}}/\rho_{\text{ox}}$ is the equivalent volume of oxide formed (M_{ox} being its mass per equivalent and ρ_{ox} its density) and $M_{\text{m}}/\rho_{\text{m}}$ is the equivalent volume of metal (or oxide) which has disappeared. The expansion coeffi-

TABLE 3

Activation energies for the oxidation of the base metals in air

Base metal	Temperature region (°C)	Activation energy (kcal mol ⁻¹)
Ti	450–800	42
Zr	380–700	33
Nb	250–390	22
Ta	270–500	29
Nb-1% Zr	340–400	23
Ta-40% Nb	360–450	20

TABLE 4
Expansion coefficients (Δ) for oxides of different valve metals

Metal	Reactions	Δ
Ti	$\text{Ti} + 1/2\text{O}_2 = \text{TiO}$	1.22
	$2 \text{TiO} + 1/2\text{O}_2 = \text{Ti}_2\text{O}_3$	1.20
	$\text{Ti}_2\text{O}_3 + 1/2\text{O}_2 = 2 \text{TiO}_2$ (anatase)	1.33
Zr	$\text{Zr} + \text{O}_2 = \text{ZrO}_2$ (zirconia C)	1.54
Nb	$\text{Nb} + 1/2\text{O}_2 = \text{NbO}$	1.38
	$\text{NbO} + 1/2\text{O}_2 = \text{NbO}_2$	1.40
	$2 \text{NbO}_2 + 1/2\text{O}_2 = \text{Nb}_2\text{O}_5(\alpha)$	1.40
Ta	$\text{Ta} + 1/2\text{O}_2 = \text{TaO}$	1.20
	$\text{TaO} + 1/2\text{O}_2 = \text{TaO}_2$	1.64
	$4 \text{TaO}_2 + \text{O}_2 = 2 \text{Ta}_2\text{O}_5$	1.26

coefficients calculated for several oxide formation reactions are given in Table 4. All the values are greater than unity, suggesting the presence of internal mechanical stresses in the lateral side sections of the oxide layer. Above a critical temperature, these stresses are no longer compensated by the plasticity of the oxide and may cause fractures, slidings and even exfoliation of the oxide. The oxidation reaction rate is therefore increased, resulting in discontinuity and higher slopes for the Ta and Nb compounds (Fig. 3).

From the calculated activation energies the valve metals and their alloys can be classified in the following sequence as regards oxygen affinity



To determine the maximum temperature for each valve metal (the critical temperature), thermogravimetric measurements were carried out in air by increasing the temperature linearly with time at $2^\circ \text{C min}^{-1}$ and recording the increase in weight of the samples (Fig. 4). The inflection points of the curves, indicated by the white circles, give the critical temperature in air above which the oxidation rate of the valve metals increases considerably. The temperature required for the coating deposition should never be above this critical temperature; otherwise a brittle or insulating interface will form between the coating and the base metal, leading to an inert electrode.

Chemical and electrochemical stability of the base metal

Microphotographs of the DSA electrodes show many cracks on the surface of the coating (Fig. 5). The presence of such cracks indicates that the coating is porous, and this is confirmed by other data obtained with $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings deposited on non-valve base metals. When these electrodes are anodized in 1 M H_2SO_4 and 1 M NaOH at 300 mA cm^{-2} , it is found that the service life depends directly on the chemical and electro-

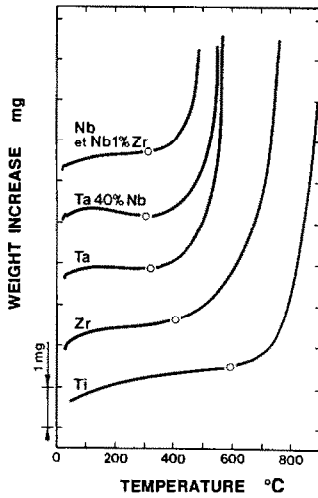


Fig. 4. Thermogravimetric curves of base metals obtained in air by increasing the temperature linearly with time at $2^{\circ}\text{C min}^{-1}$.

chemical stability of the base metals used (Table 5). As a matter of fact, it is well known that nickel and stainless steel dissolve in acidic solution but are stable in alkaline solution, while aluminium dissolves in both acidic and alkaline solutions. This fact clearly indicates that the electrolyte passes through the cracks or pores of the coating to reach the surface of the base metal, resulting in its corrosion and/or passivation.

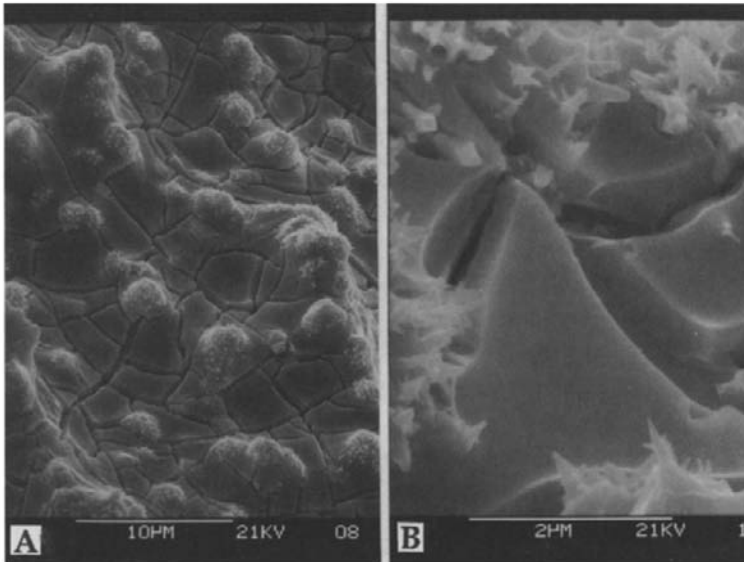


Fig. 5. Microphotographs of a $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$ anode: A, $\times 5000$; B, $\times 14000$.

TABLE 5

Service life of the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coating on different nonvalve base metals

Non-valve base metal	Service life measured in minutes	
	1 M H_2SO_4	1 M NaOH
Aluminium	2	13
Stainless steel	6	> 2880
Nickel	13	> 2880

Chemical stability

Many papers have been published concerning the chemical stability of valve metals in different media [11,12,13]. Figures 6 and 7 show data, collected from different sources, of iso-corrosion curves and corrosion rates of the valve metals as a function of temperature and H_2SO_4 concentration.

Electrochemical stability

The electrochemical stability of the valve metals has been tested in different H_2SO_4 concentrations, at 80°C , under potentiostatic conditions by anodic polarization at 2V ($\text{Hg}/\text{Hg}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ satd.). The results obtained

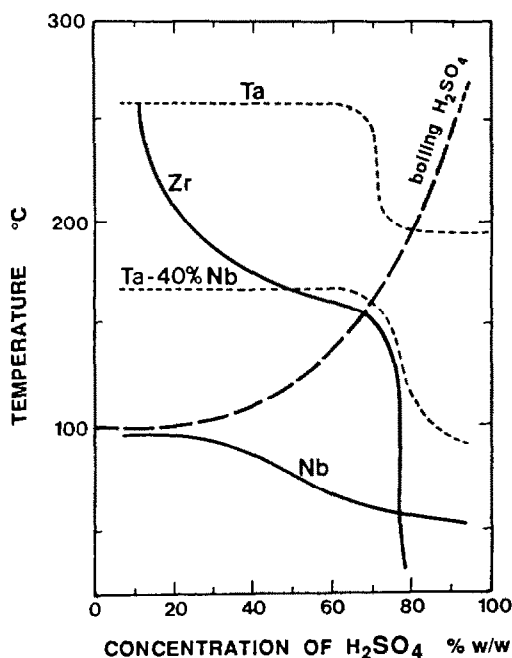


Fig. 6. Iso-corrosion curves (0.125 mm yr^{-1}) of base metals in H_2SO_4 as a function of temperature.

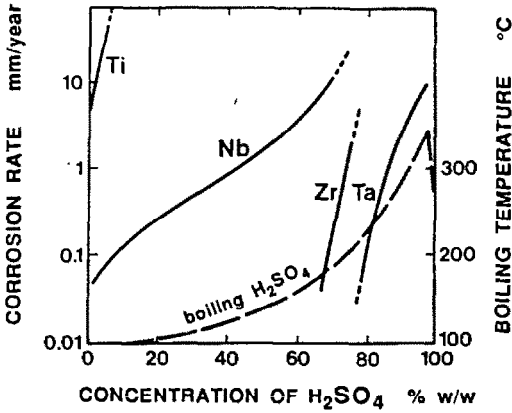


Fig. 7. Chemical corrosion rate of the base metals in boiling H₂SO₄.

from the loss of weight of the samples are given in Fig. 8. Comparison of the chemical and electrochemical stabilities of the valve metals studied shows that these metals are much more stable under anodic polarization. Therefore, the electrode should always be kept polarized to prevent chemical corrosion.

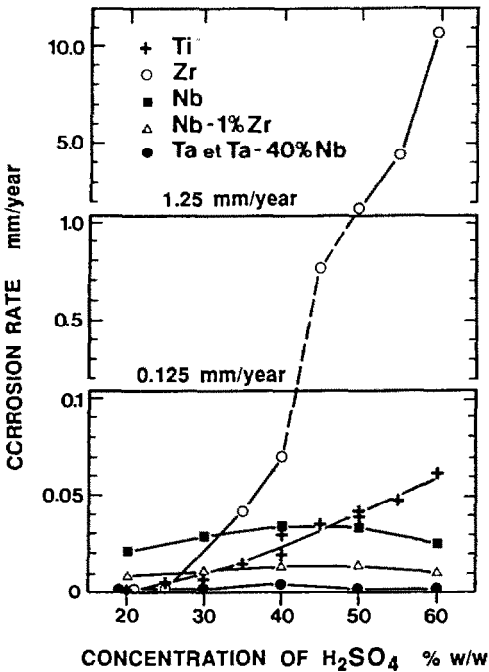


Fig. 8. Electrochemical corrosion rate of the base metals as a function of H₂SO₄ concentration at anode potential of 2 V (vs. Hg/Hg₂SO₄·K₂SO₄ satd.).

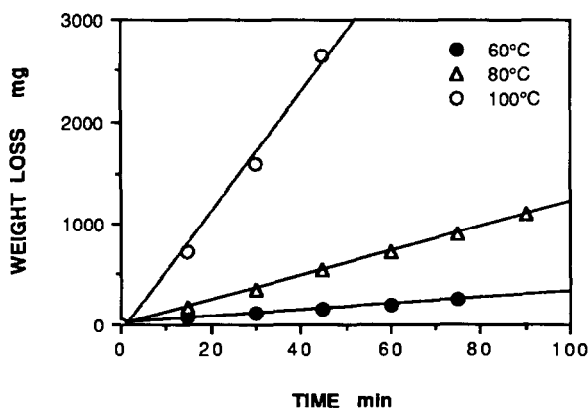


Fig. 9. Pretreatment of titanium samples by etching in 32% HCl at different temperatures; weight loss of titanium as a function of time (surface of each sample: 100 cm²).

It is important to note that the electrochemical corrosion rate determined for the valve metals, obtained without coating, are much higher than the values obtained for anodically polarized valve metals coated with IrO₂-Ta₂O₅ (see section on service life measurements below).

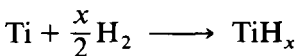
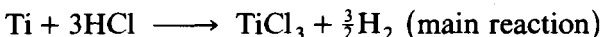
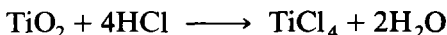
Pretreatment of the base metal

To achieve good adhesion of the coating, the surface of the base metal must be pretreated to an appropriate degree of roughness. The mode of pretreatment depends strongly on the nature of the base metal.

Titanium

Titanium base metal is generally pretreated by sandblasting, then etched in hot concentrated HCl or in oxalic acid. The weight loss of titanium treated in 32% HCl at different temperatures is shown in Fig. 9. From this figure the corrosion rate of titanium in 32% HCl as a function of temperature can be determined (Fig. 10).

Etching of titanium in HCl involves three main processes: oxide dissolution, metal dissolution (main reaction) and hydride formation



The surface of titanium after pretreatment in HCl has an appropriate degree of roughness, caused by pitting corrosion (Fig. 11A).

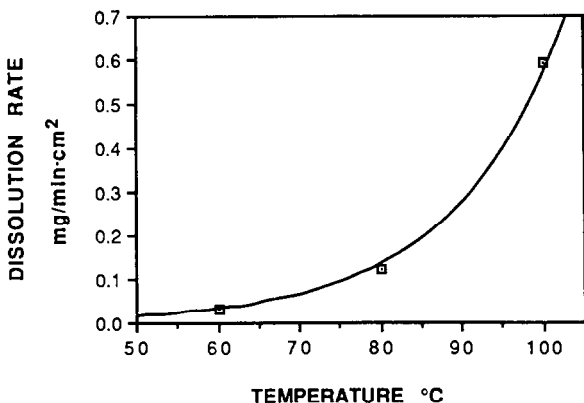


Fig. 10. Etching rate of titanium in 32% HCl as a function of temperature.

Etching of titanium in oxalic acid produces Ti^{4+} (contrast etching with HCl where Ti^{3+} is formed).

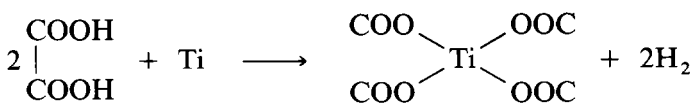


Figure 12 shows the weight loss of titanium treated with 10% oxalic acid at different temperatures and Fig. 11B shows the morphology of the surface obtained. This appears to be a little smoother compared with HCl etching, but is rough enough for coating adhesion.

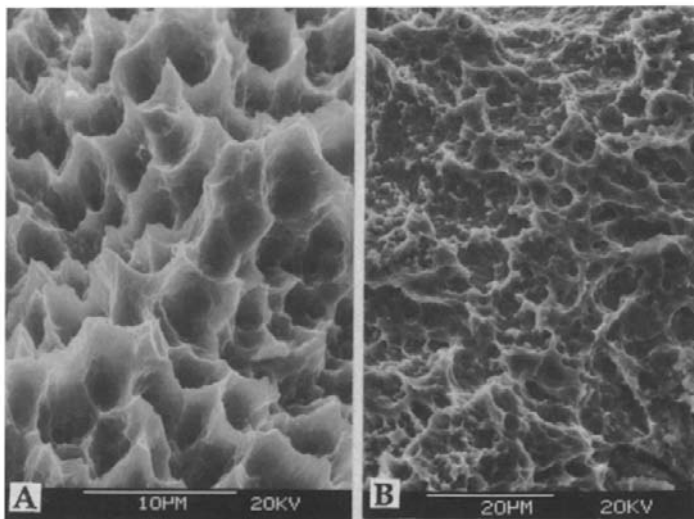


Fig. 11. Microphotographs of titanium after etching in: A, 32% HCl; B, 10% oxalic acid.

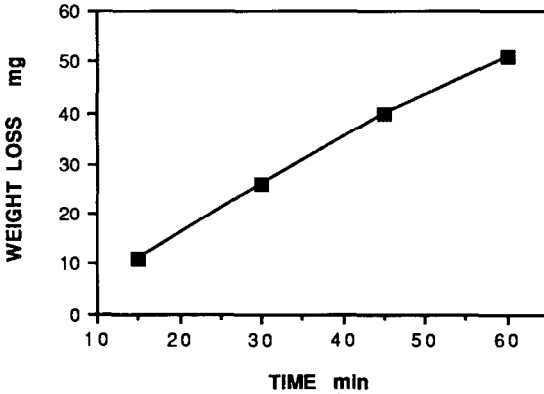


Fig. 12. Pretreatment of sandblasted titanium in 10% oxalic acid at 85°C; weight loss of titanium as a function of time (surface of each sample: 100 cm²).

Zirconium

Zirconium is rarely used as base metal and there is no information concerning its pretreatment before coating application. To find the appropriate pretreatment, zirconium was sandblasted, then treated in various etching media. Table 6 shows that the etching agents used have little or no effect on the surface roughness and microphotographs show that there is no noticeable difference between sandblasted samples and those additionally subjected to etching. We note that when zirconium is treated in aqua regia, its surface appears to be polished.

Tantalum

The highest roughness for tantalum was obtained by sandblasting then treating in 40% HF at 25°C for about 1 h. Etching of tantalum in HF involves two main processes: oxide dissolution and metal dissolution.

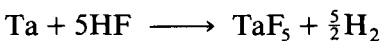
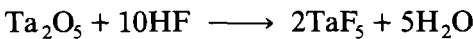


TABLE 6

Influence of etching agents on the surface morphology of zirconium

Etching agent	Time	Temperature (°C)	Surface
20% FeCl ₃	1 h	80	unchanged
20% CuCl ₂	1 h	80	unchanged
10% CCl ₃ COOH	1 h	100	unchanged
Aqua regia	10 s	20	polished
5% HF-45% HNO ₃	10 s	20	unchanged

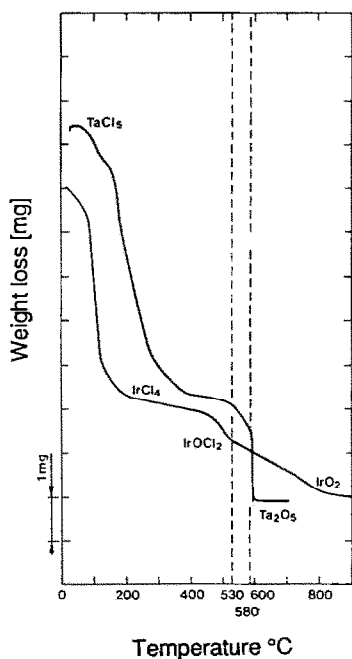
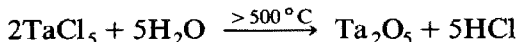
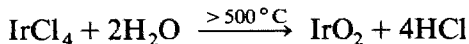
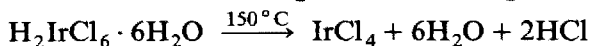


Fig. 13. Thermogravimetric curves of coating agents obtained in air at a heating rate of $2^{\circ}\text{C min}^{-1}$.

Thermal decomposition of the coating agents

The thermogravimetric curves of $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ and TaCl_5 (coating agents) obtained in air are shown in Fig. 13. This figure shows that the decomposition of the coating agents to the corresponding oxides occurs above 500°C according to the following reactions



The decomposition temperature of the coating agents is higher than the critical temperature in air of all the valve metals, with the exception of titanium. To overcome this problem, the thermal treatment has been carried out in argon atmosphere saturated with water.

Service life measurements

Typical potential–time curves for the $\text{IrO}_2\text{--Ta}_2\text{O}_5$ coating on different base metals are shown in Fig. 14. Evidently the service life depends on the nature of the base metal. In the case of zirconium, a sharp increase in potential is observed after about 5 h; titanium also shows a sharp increase in

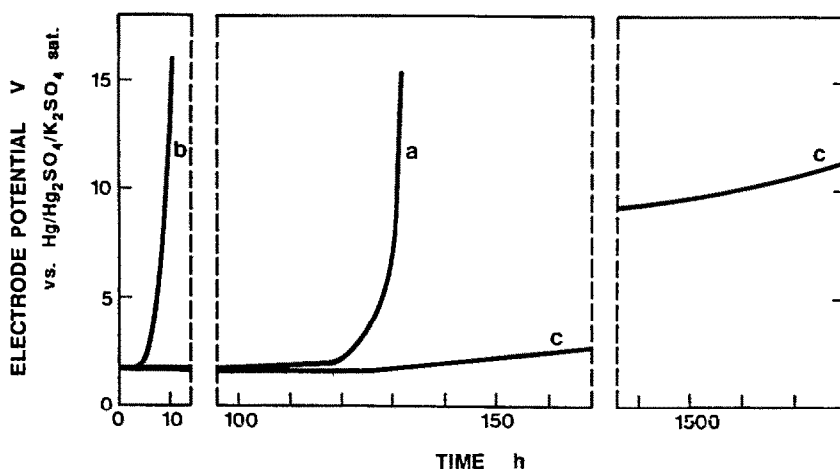


Fig. 14. Potential-time curves during service life test of 70% IrO_2 -30% Ta_2O_5 coatings deposited on: a, titanium; b, zirconium; and c, tantalum base metals.

potential but after about 120 h. Tantalum, however, has a long service life and its potential increases only slowly with time.

The service life of the IrO_2 - Ta_2O_5 coating on different base metals can be related to the electrochemical stability of the base metal. The higher its electrochemical stability (low corrosion rate), the longer the service life of the coating (Fig. 15). The base metal corrosion rates given in Figs. 15 and 16 are calculated from the dissolved metal ions content of the electrolytic solution. Because of the acidification of the anode/electrolyte interface during oxygen evolution, the corrosion rates for titanium (0.14 mm yr^{-1}) and zirconium (1.00 mm yr^{-1}) are higher than the values obtained in the electrochemical stability tests with uncoated valve metals (0.01 and 0.02 mm yr^{-1} , respectively, from Fig. 8).

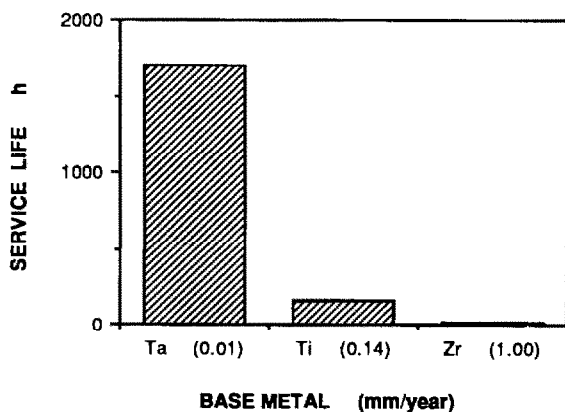


Fig. 15. Influence of the base metal (and its corrosion rate) on the service life of the 70% IrO_2 -30% Ta_2O_5 coating.

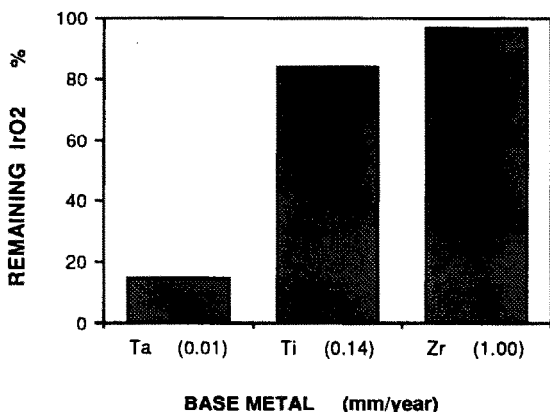


Fig. 16. Amount of IrO₂ remaining at the end of the service life of IrO₂-Ta₂O₅ coatings deposited on different base metals (the amount of Ta₂O₅ remains constant).

From microphotographs and fluorescence X-ray analysis of the coating at the end of the service life test, the amount of coating remaining was estimated (Fig. 16). For tantalum-based electrodes, most of the IrO₂ in the coating had been dissolved, but with zirconium the amount of IrO₂ remains almost unchanged at the end of service life.

On the basis of the present results, two main factors contribute to the activity loss of DSA-O₂ electrodes: dissolution of the coating (at a rate ν_1) and dissolution or/and passivation of the base metal (at a rate ν_2). If the dissolution rate of the coating is higher than that of base metal ($\nu_1 > \nu_2$), then coating dissolution determines the service life of the electrode (e.g. where tantalum is the base metal), but if $\nu_2 > \nu_1$, the base metal dissolution or/and passivation determines the service life of the electrode (e.g. where zirconium is the base metal).

CONCLUSIONS

The results obtained in this investigation, aimed at examining the behaviour of a M/IrO₂-Ta₂O₅ electrode (M is a valve metal) in accelerated lifetime tests (30% H₂SO₄; 80 °C; 750 mA cm⁻²), have demonstrated the following.

(1) The electrode preparation conditions (i.e. firing temperature, and oxygen content in the oven atmosphere) must be carefully controlled in order to prevent the build up of a non-adherent, non-conducting layer on the base metal surface, and base metal pretreatment by chemical etching is an essential step in generating adequate surface roughness and thus good adherence of the coating.

(2) The $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings are porous, like most DSA-type coatings, and because of this the service life of the electrodes will depend on the relative rates of coating corrosion and base metal corrosion (or passivation).

(3) Replacement of titanium by tantalum as base metal improves the service life of a $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coating, during oxygen evolution from sulphuric acid medium, by a factor of 14.

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