

Problems in DSA[®] coating deposition by thermal decomposition

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Several DSA[®] coatings were prepared by thermal decomposition of metallic chloride salts on titanium base. It was shown that the painting composition does not necessarily correspond to the final coating composition. Thermogravimetric and fluorescent X-ray measurements were used to identify and characterize the material losses. It was found that IrO₂, Ta₂O₅ and RuO₂ compounds can be deposited with almost 100% yield, while SnO₂ and Pt precursors give high material losses. The influence of parameters affecting the deposition yield are discussed.

1. Introduction

Since the discovery by Beer, about 25 years ago [1, 2], much work has been done on dimensionally stable anode (DSA[®]) electrodes. The studies have mainly focused on Ti/RuO₂-TiO₂ anodes, very popular in the chlor-alkali industry. These electrodes, however, exhibit very poor performances when used as oxygen evolution anodes. Nevertheless, their good performances in chloride solutions suggested that, with an appropriate coating, a new DSA[®] could be found for oxygen evolution. This motivated intensive research in our laboratory [3, 4-6] which lead to the Ta/IrO₂-Ta₂O₅ electrode.

A DSA[®] electrode is composed of an electrochemically active coating, deposited on a base metal. The coating is generally a binary mixture of oxides, one of which is conducting and the other inert: the general form is then Me/AO_x-BO_y, where Me is the base metal, AO_x the conducting oxide and BO_y the inert oxide of the coating. The conducting oxide should have a good catalytic activity towards the desired reaction, and a good chemical and electrochemical corrosion resistance; the non-conducting oxide should ensure a high dispersion of the catalyst, protect the base metal from corrosion and strengthen the cohesion of the coating.

The composition of the coating, and the ratio between the conducting and inert oxides, strongly influences the morphology, the structure (e.g. in the case of solid solutions), the activity and the operating time, i.e. the whole electrochemical behaviour of the electrode. It is therefore a fundamental necessity to know the exact composition of the coating, before going into speculative interpretations about the correlation between structure and performance.

In the standard thermal decomposition preparation technique [7], appropriate amounts of the metal salt are dissolved to form a painting solution which is applied by brush, spray or dipping onto a base metal; the solvent is evaporated at low temperatures and the

oxides are formed at high temperature (typically 400° to 550° C). In the literature, the composition of the coating is always calculated from the components dissolved in the painting solution, thus assuming that all the applied material is transformed to the corresponding oxides, with a deposition yield of 100%. Some experiments presented in this paper will show that this is not always the case. Some authors [1, 8, 9] have checked the coating composition mainly by Auger analysis, which only gives an analysis to a few nanometres depth in the sample, and may not reflect the composition of the bulk of the coating, which is usually several micrometres thick. In general it appears that the correspondence between the painting solution and the effective coating composition, has been largely overlooked.

It is not the purpose of this paper to study the deposition of all known DSA[®] coatings, but to show that the deposition yield is a very important factor, particularly when a mechanism or property of a coating is interpreted on the basis of its chemical composition or structure. In this work IrO₂, Ta₂O₅, SnO₂, RuO₂-SnO₂ and PtO_x coatings were studied through deposition yields, thermogravimetric measurements and fluorescent X-ray analysis in different conditions. IrO₂-Ta₂O₅ coatings are of commercial importance in applications where oxygen evolution is promoted from acidic media; platinum is also used in a wide range of different technological applications: it is therefore of major interest to characterize their deposition procedure.

In DSA[®] technology, tin oxide has been mainly used together with antimony as doping agent, as inhibitor for the oxygen evolution reaction during sea water electrolysis, with Ti/RuO₂-TiO₂ anodes [1]. Some studies [10, 11, 12] have demonstrated the ability of SnO₂ to increase considerably the electrochemical stability of RuO₂ and IrO₂-RuO₂ coatings. Recent needs for optically transparent electrodes (mainly in photo-electrochemistry) prepared by thermal decomposition [13] motivated the study of SnO₂ coating deposition.

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Table 1. Deposition yields and preparation conditions for some coatings

Metal salts	Solvent	Conc. (M)	No. of coatings	Annealing temp. (° C)	Formed oxide	Deposition yield (%)
H ₂ IrCl ₆ ·6H ₂ O	20% HCl	0.09	7	550	IrO ₂	100
	20% HCl	0.09	14	550	IrO ₂	100
	<i>i</i> -PrOH	0.177	10	550	IrO ₂	97 ± 2
H ₂ IrCl ₆ ·6H ₂ O + TaCl ₅	EtOH-	0.136	10	550	IrO ₂ + Ta ₂ O ₅	98 ± 4
	<i>i</i> -PrOH (1:1)	0.102				
SnCl ₄	20% HCl	4.25	3	400	SnO ₂	15
	EtOH	2.82	3	400	SnO ₂	21
SnCl ₂	20% HCl	1.4	3	550	SnO ₂	66
	EtOH	1.4	3	550	SnO ₂	57
H ₂ PtCl ₆ ·6H ₂ O	H ₂ O (90%)	0.5	14	500	PtO _x (x ≤ 0.18)	58
	EtOH (10%)					

2. Experimental details

2.1. Coating preparation

In the standard thermal decomposition preparation technique, appropriate amounts of the metal salts are dissolved in a suitable solvent to form a painting solution. The latter is applied by brush onto a base metal (titanium) in a certain number of sequential coatings, each layer being dried for 10 min at 80° or 100° C in order to evaporate the solvent, then fired for 5 min in air at high temperature (typically 450° to 550° C). After the last layer, the coating is additionally annealed at the same high temperature for 1 h.

2.2. Deposition yields

The painting solution is weighed before and after each layer deposition, which allows calculation of the theoretical weight increase of the sample. It is assumed that only the most common, pure, stoichiometric oxide is formed. The deposition yield is obtained by comparing this, with the effective, as measured, weight increase of the samples. Impurities and Cl⁻ ions, which have been found by Auger analysis, are nevertheless neglected in the mass balances. Small percentage losses occur when organic solvent is used due to the high volatility of the alcohol: each time the tap of the solution bottle is opened, small quantities of solvent evaporate causing a small overestimation of the deposited material. Only corrected results will be given here.

2.3. X-ray fluorescence analysis

Samples of titanium coated with different coatings were uniformly irradiated with an americium-241 source (γ -emission of 59.6 keV); analysed surface: 6.51 cm²; counting time: 5000 s with a resulting error on the integral of the peak of 0.5% for Ru and 2.6% for Sn.

2.4. Thermogravimetric measurements

A Mettler 197 electromagnetically compensated thermobalance was used. A platinum or aluminium crucible containing the samples of metal chloride was heated in air and the changes in weight were recorded as a function of temperature, for a linear increase of temperature with time of 1° C min⁻¹.

3. Results

3.1. IrO₂ coatings

Table 1 gives the deposition yields obtained from different solutions of H₂IrCl₆·6H₂O, applied on Ti base, treated at 550° C. It shows that all the deposited material is converted to the corresponding oxide IrO₂. The annealing temperature of 550° C was chosen on the basis of thermogravimetric experiments [6].

3.2. IrO₂-Ta₂O₅ coatings

Similarly, Ta₂O₅ can be applied with approximately 100% yield, and thus a painting solution of H₂IrCl₆·6H₂O and TaCl₅ in ethanol-isopropanol mixture, can be deposited with high yields (Table 1): > 95% on Ti base, which correspond to 98 ± 4% if losses due to the volatility of the solvent are compensated. This coating and its preparation conditions correspond to the Ti/IrO₂-Ta₂O₅ electrode studied in our laboratory for oxygen evolution in acidic media [3, 4].

Figure 1 shows the weight of material deposited at each layer application, for 9 electrodes: the relation is a straight line, and all the correlation coefficients are greater than 0.996 indicating that the material deposited is constant, i.e. the coating deposition procedure by brush is reproducible from layer to layer. On the other hand from electrode to electrode, the experimental error is between 15 and 20%. The mean slope of all the straight lines is 1.84 ± 0.06 mg per layer (mean surface for each sample: 5.8 cm²). A Ti

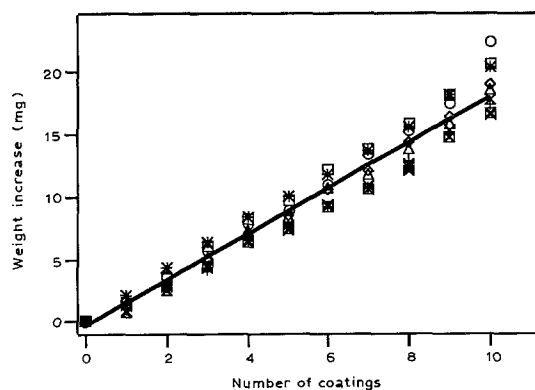


Fig. 1. Weight increase of IrO₂-Ta₂O₅ coatings, as a function of the number of applied layers. Preparation conditions are reported in Table 1.

electrode, without coating, following the same thermal treatment, showed that the weight increase due to the formation of titanium oxides can be neglected.

3.3. SnO₂ coatings

The deposition yields obtained with different tin containing compounds dissolved in different solvents are given in Table 1. Experiments with SnCl₄ show that deposition yields are extremely low, which is undoubtedly due to the low boiling point of the chloride (114°C, see Table 2): at the drying temperature of 100°C, the vapour pressure of the freshly applied painting is near atmospheric pressure, causing high material losses, and in fact a soft white powder deposit of SnO₂ is found on the walls of the oven.

As will be discussed later, the use of alcohol instead of water improves the wettability of the painting solution and leads to an organometallic complex, which acts as a stabilizing agent, giving higher deposition yields.

The above considerations prompted a search for a more stable tin containing chloride salt. SnCl₂ was chosen for its relatively high melting and boiling point (see Table 2), and effectively the deposition yields were much higher.

Table 2. Physical properties of some metal chlorides used in the preparation of coatings

Metal salt	Melting point (°C)	Boiling point (°C)	Decomposition* (°C)
SnCl ₄	—	114	—
SnCl ₂	246	652	—
SnCl ₄ ·5H ₂ O	—	—	460
H ₂ PtCl ₆ ·6H ₂ O	60	—	480
H ₂ IrCl ₆ ·6H ₂ O	?	?	550
RuCl ₃	—	—	505
TaCl ₅	216	242	580

* Oxide formation temperature, from thermogravimetric data [3, 4].

3.4. Pt coatings

Thermogravimetric measurements of H₂PtCl₆·6H₂O have shown that the final product obtained by heating up to 800°C is PtO_x (with $x < 0.2$). The deposition yields are therefore calculated in respect to Pt and not PtO₂. Tables 1 and 2 show that the high volatility of the Pt compound is again responsible for the low depositions obtained.

3.5. Mixed coatings

Table 3 gives the results of the different binary oxides tested. It is shown that all mixtures containing either Pt or Sn give a global lower deposition yield than for pure IrO₂ or Ta₂O₅. As expected yields of IrO₂-SnO₂ coatings prepared with SnCl₂ are higher than with SnCl₄.

The low deposition yields for SnO₂ and Pt have not been taken into consideration in a number of papers and it seems that some of the results obtained in the literature should be reinterpreted on a new basis. As an example, the indium-tin oxide thin films prepared by thermal decomposition, show a minimum in the electrical resistivity for a certain painting solution composition [13]: because of probable Sn losses, this is

Table 3. Deposition yields and preparation conditions for some binary coatings, containing either Sn or Pt

Metal salts	Solvent	Conc. (M)	No. of coatings	Annealing temp. (°C)	Formed oxides	Deposition yield (global) (%)
H ₂ PtCl ₆ ·6H ₂ O + H ₂ IrCl ₆ ·6H ₂ O	<i>i</i> -PrOH	0.5 0.14	10	550	IrO ₂ + Pt	84
H ₂ IrCl ₆ ·6H ₂ O + SnCl ₄	20% HCl	0.04 0.34	10	550	SnO ₂ + Pt	49
H ₂ IrCl ₆ ·6H ₂ O + SnCl ₂	20% HCl	0.03 0.1	3	550	IrO ₂ + SnO ₂	68
SnCl ₂ + TaCl ₅	<i>i</i> -PrOH	2.08 0.21	3	550	SnO ₂ + Ta ₂ O ₅	56
SnCl ₂ + SbCl ₅	20% HCl EtOH	0.1 0.126	3	550	SnO ₂ + Sb ₂ O ₅	35

most likely to be different from the real In-Sn ratio obtained in the annealed coating.

Another typical example is the RuO₂-SnO₂ coating for which a maximum of service life was obtained with a painting solution composition of 30 mol % Ru-70 mol % Sn which was explained by the formation of an RuSn₂O₆ compound [10].

We decided to study this coating in more detail. In order to get a more specific evaluation of the deposited material than the weight increase, we used fluorescent X-ray analysis, which is non destructive, specific for each metal element and is also capable of analysing large surfaces (up to 6.5 cm²); the in-depth penetration of the incident beam is a few micrometres (3 to 4 μm) and therefore, this analysis is not limited to the very surface but accounts for the total coating thickness (typically 1 to 1.5 μm). Calibration curves for each metal were obtained by preparing coatings with painting solutions containing only one metal chloride at different concentrations: the correlations between the weight increase (converted into moles of oxide) and the integral of the peak of the corresponding metal are obtained. Mass balances on the pure coatings showed that a 10 to 20% yield is obtained with the tin compound, while 94 to 100% yields are obtained with ruthenium chloride. The actual amounts of Sn and Ru deposited in the binary coatings Ru-Sn, are calculated from the calibration curves. The experimental points are reported in Fig. 2, which shows the correspondence between the composition of the solution and the actual composition of the coating: the points are largely shifted towards an Ru concentration increase in the coating, and can be approached by a theoretical curve (plain curve) that has been calculated by considering a 100% deposition yield for RuO₂, and 10% for SnO₂. The straight line shows the theoretical correspondence if 100% deposition is achieved with both RuO₂ and SnO₂.

X-ray diffraction experiments were performed on various coatings containing different concentrations of Ru. Figure 3 shows that no significant Ru peak displacement was found, and thus no solid solution is formed, contrary to [10].

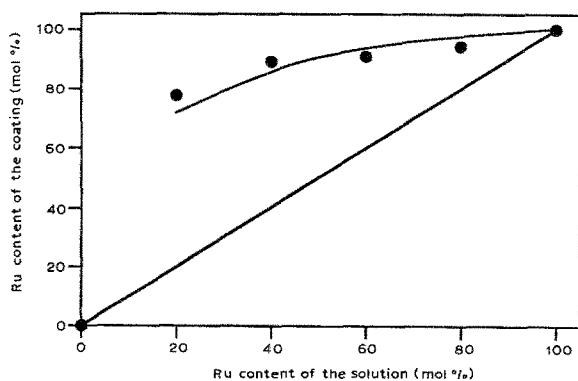


Fig. 2. Painting solution composition versus the real coating composition. The dots indicate the experimental data obtained by fluorescent X-ray analysis; plain line curve: calculated with 10% yield for Sn and a 100% yield for Ru; straight line: calculated with 100% yield for both Sn and Ru.

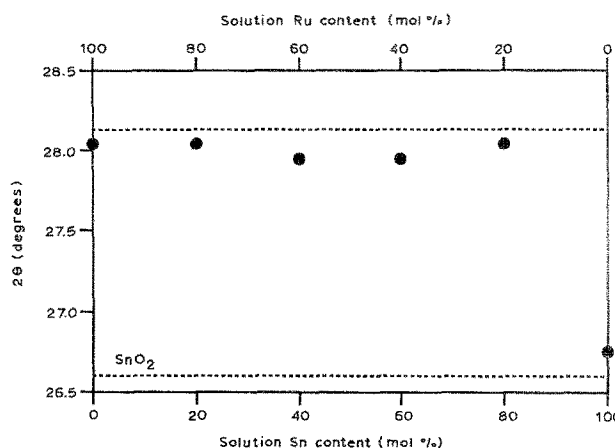
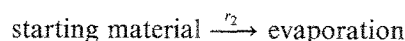
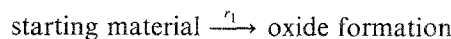


Fig. 3. Plot of X-ray diffraction angle of the RuO₂-SnO₂ coating against the Ru content of the painting solution.

4. Discussion

4.1. Deposition yields

All the results concerning low deposition yields must be understood in terms of relative rates of decomposition r_1 (i.e. oxide formation) and evaporation r_2 (i.e. losses).



The drying step in the preparation procedure is necessary to evaporate the solvent. This is a first critical point of the procedure, because part of the material can evaporate if its boiling (or sublimation) point is too low: this is probably the case with SnCl₄. The second step is the firing of the sample at high temperature, which can be the origin of another loss of material. At this stage two competitive reactions may take place: the oxide formation and the evaporation of the compound. The deposition yield is high if the rate of decomposition (to the oxide) is higher than the rate of evaporation of the material.

The decomposition rate, r_1 , depends on thermodynamic and kinetic data: temperature, Gibbs' enthalpies, activation energy, rate constant, relative concentrations of the species (metal chloride and oxygen); while r_2 depends on the physical properties of the metal chloride: melting point, boiling point, sublimation point (if any), vapour pressure at the treatment temperature, and also the surface tension of the applied painting solution, which can be varied by use of an appropriate solvent.

4.2. Case of RuO₂-SnO₂ coating

On the basis of the results obtained with the RuO₂-SnO₂ coatings, the formation of an RuSn₂O₆ compound, as proposed previously [10], seems rather speculative and more direct evidence is required. We have found that the coating composition is always > 78 mol % in Ru. The losses in deposition of Sn

compounds may be interpreted in terms of oxygen deficiencies: but our fluorescent X-ray measurements clearly established that the main losses are due to Sn losses. On the other hand we found that the characteristic peak of rutile SnO_2 is only present in the 100% SnO_2 coating. As suggested by Hutchings *et al.* [11], SnO_2 is not thought to be soluble in RuO_2 , the ionic radius of Sn^{4+} (0.083 nm) being considerably larger than for Ru^{4+} (0.076 nm). However, it cannot be completely ruled out on the basis of the Hume-Rothery rule, and some clustering is still possible.

4.3. Comments on the validity of thermogravimetric measurements

How does one determine the annealing temperature necessary for a coating preparation? In the field of DSA[®] electrode preparation, knowledge is a matter of experience and usually the preparation procedure given either by early publications or directly by a manufacturer is followed. But originally (for Ru see [14, 15]), the annealing temperatures were determined by thermogravimetric measurements of the single metal chloride, which give the temperatures of the different decomposition steps. It was found that the most common salts (of Ru, Ir, Ti, Pt, Ta) need the temperature range 350° to 500° C. When a new compound is chosen, its thermal behaviour should be determined, in order to find the most appropriate annealing temperature. The problem is, of course, more delicate when the coating is a mixture of two oxides with very different decomposition temperatures.

The oxide formation at high temperatures occurs through a hydrolysis (e.g. $\text{SnCl}_4 \rightarrow \text{SnO}_2$) or oxidation (e.g. $\text{SnCl}_2 \rightarrow \text{SnO}_2$) mechanism and the former can be promoted in two different ways: by heating the chloride in a water containing atmosphere, or by heating the hydrated salt. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is, therefore, a good candidate and Fig. 4 shows the thermogram recorded at a speed of 1°C min^{-1} . From

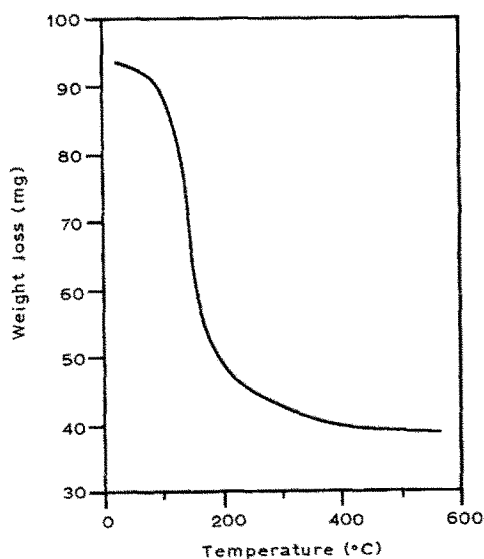


Fig. 4. Thermogravimetric measurement of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Rate of temperature increase: 1°C min^{-1} .

Table 4. Deposition yields of SnCl_4 in acetylacetone, as a function of the sample geometry

Compound	Solvent	Mode of decomposition	Formed oxide	Conversion yield
SnCl_4	acetylacetone	crucible	SnO_2	82%
SnCl_4	acetylacetone	crystallizer	SnO_2	56%
SnCl_4	acetylacetone	flat surface (7.5 cm ²)	SnO_2	30%

weight loss calculations, it can be shown that 100% of the initial salt is converted into its oxide. Thus a 100% deposition yield is expected to electrodes with a temperature treatment at 460° C. However, coatings prepared on Ti base at 460° C with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in ethanol, gave only very low deposition yields.

Discrepancies between these results must arise from differences in the surface geometry of the compound exposed to the hot atmosphere (use of a crucible in thermogravimetry, instead of an open surface in the case of electrodes), and the use of a solvent in real coating preparation.

In order to get more insight into this phenomena, we measured the deposition yields of SnCl_4 dissolved in acetylacetone, and deposited in a narrow crucible (2.5 cm diameter, 4 cm high), in a crystallizer (4.5 cm diameter, 2.7 cm high) and on a free surface (2.5 cm × 3 cm plaque). The results given in Table 4 show that the deposition yields are very sensitive to the surface of metal chloride exposed to the atmosphere. This indicates that the hydrolysis or oxidation processes are slow: in thermogravimetry where, generally, low heating rates are used (typically 1°C min^{-1}), and where the compound, in the form of powder (grains), is put in a Pt or Al crucible (5 mm diameter, 8 mm high), the water or oxygen content of the firing atmosphere (mostly air) is sufficiently high to react and form an oxide film covering the grain surface. The evaporation is, therefore, inhibited and the treatment leads to 100% conversion of the chloride. In the case of DSA[®] coating preparation, the same compound is submitted to a thermal shock when introduced into the furnace, and it seems probable that the SnCl_4 evaporates readily. If the painting is spread on a large open surface, the chloride evaporates faster.

The use of a solvent in the coating preparation is also a source of differences with the thermogravimetry. This has already been suggested for Ru-Ti coatings [15]. To see if the fact of dissolving the salt alters the thermogravimetric properties of the compound, we recorded the thermograms of pure $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and TiCl_3 (Figs 5 and 6). Then we dissolved comparable amounts of each salt in an organic mixture (ethanol-isopropanol), dried at 80° C for 15 min, and finally recorded new thermograms (Figs 5 and 6). The same procedure was followed with an alcoholic solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ mixed with TiCl_3 (Fig. 7). The curves are very different with or without solvent: the decomposition steps and the temperatures at which decomposition occurs, clearly indicate that organometallic complexes are formed which follow a

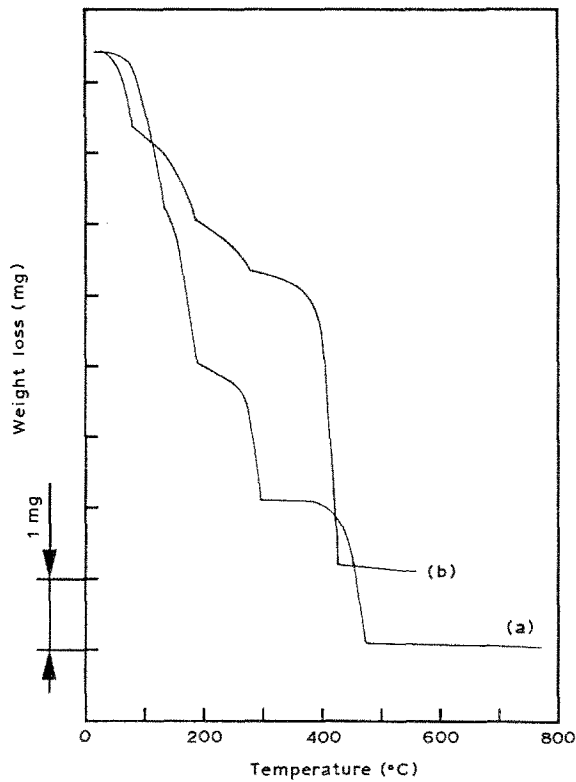


Fig. 5. Thermogravimetric measurement of $H_2PtCl_6 \cdot 6H_2O$: (a) pure; (b) previously dissolved in alcoholic solution, then dried at low temperature.

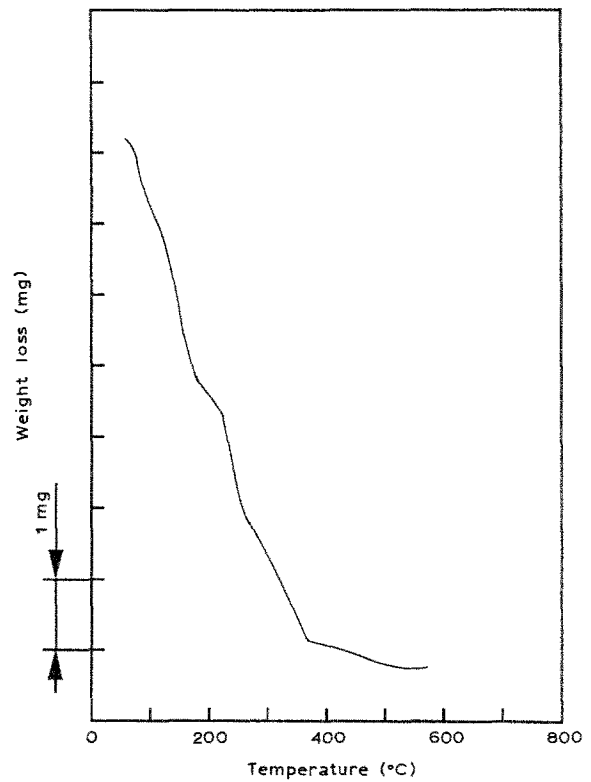


Fig. 7. Thermogravimetric measurement of a mixture of $H_2PtCl_6 \cdot 6H_2O$ and $TiCl_3$ previously dissolved in alcoholic solution, then dried at low temperature.

very different path to the oxide formation to that expected.

It is interesting to note, in the case of $H_2PtCl_6 \cdot 6H_2O$ previously dissolved in alcohol, that the decomposition temperature is lowered significantly from 480 to 420°C (leading in both cases to $PtO_{0.18 \pm 0.12}$).

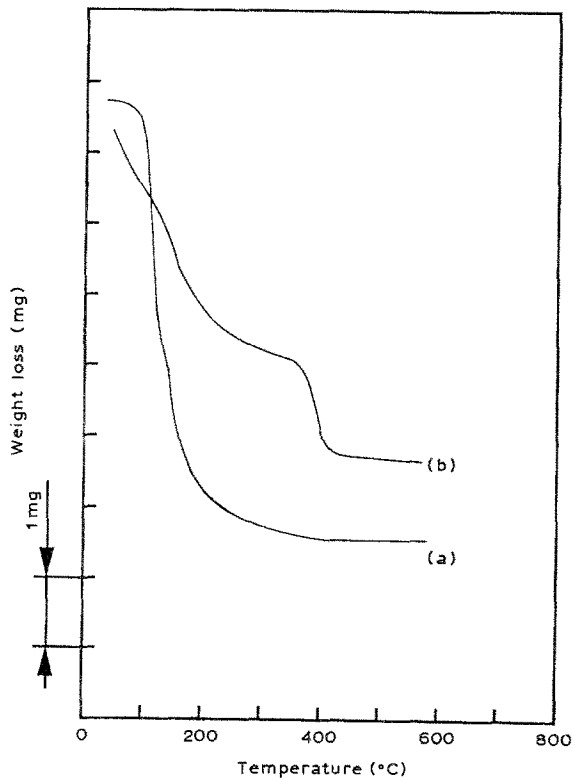


Fig. 6. Thermogravimetric measurement of $TiCl_3$: (a) pure; (b) previously dissolved in alcoholic solution, then dried at low temperature.

The same probably happens for $SnCl_4$ in ethanol, as seen in Table 1, explaining that higher yields can be obtained through stabilization of the Sn by complexation with ethanol.

5. Conclusion

It has been shown that the deposition of tin and platinum chloride salts on a titanium substrate, with the classical thermal decomposition method, is not complete. Losses have been found to be 40 to 80 wt % for Sn chlorides and about 40 wt % for $H_2PtCl_6 \cdot 6H_2O$. In the case of binary mixtures containing either Sn or Pt, the composition of the formed coating is never the composition of the initial painting solution, and this can become a source of misleading interpretations of mechanisms and structures. The thermal decomposition technique seems to be very sensitive to the geometry of the sample, the solvent used, the concentration and the nature of the metal salts. We have shown that IrO_2 , Ta_2O_5 and RuO_2 can be deposited with almost 100% yields.

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