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Contribution to the study of the reaction of mercury with platinum and a platinum–iridium alloy

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Abstract

Thermogravimetry (TG) and other analysis techniques have been used to study the reaction of mercury with Pt and a Pt–Ir alloy. The results suggested that, when heated, the electrodeposited Hg film reacts with Pt or with Pt–Ir to form products of different stabilities, indicated by at least three weight loss steps. In the first step, between room temperature and 170°C, only the bulk Hg is removed. From this temperature to about 280°C the mass loss can be attributed to the desorption of a monolayer of mecury. The last step, from 280 to $\approx$600°C, can be ascribed to the removal of Hg from a solid solution with Pt and Pt–Ir alloy.

Keywords: Alloy; Iridium; Mercury; Platinum; TGA

1. Introduction

In recent work, pure platinum and platinum–iridium alloys have been widely used to build microelectrodes and ultra-microelectrodes [1,2]. Mercury microelectrodes are very versatile and interesting electrodes and can be used for many analytical applications [3–6]. In general, these electrodes can be prepared by the electrodeposition of mercury films on noble metals or on their alloys. These microelectrodes present some problems relating to the formation of solid intermetallic compounds mainly because these compounds form a suspension in the mercury phase and intermetallic particles appearing at the mercury surface disturb the electrode processes studied [7]. Mercury interaction with pure platinum has been investigated by means of cyclic voltammetry

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[8] and by X-ray diffraction and thermal description techniques [9,10]. The formation of a PtHg alloy and a solid solution (up to 0.23 atoms mercury per platinum atom) have been suggested [10] and the formation of $PtHg_4$ was investigated by X-ray diffraction and electrochemical techniques [11]. The formation of other compounds such as $PtHg_2$, Pt_2Hg, Pt_3Hg and bulk Hg on platinum have been mentioned [8].

In the present work, films of mercury were electrodeposited on platinum and platinum–iridium (20% w/w) foils and the thermal desorption of mercury was investigated using TG, EDX, SEM, inductively coupled argon plasma spectroscopy (ICP) and atomic absorption spectrometry with cold-vapor generation.

2. Experimental

Pt and Pt–Ir (20 wt%) foils of area 2 mm × 20 mm and 60 μm thickness were prepared: these were polished with Al_2O_3 (particle sizes < 0.3 μm) in aqueous suspension and washed in HNO_3:H_2O (50% v/v) using an ultrasonic bath. These were submitted to the following heat treatments: (a) heated at 1200°C for 4 h and quenched in oxygen-free water at 0°C; (b) heated at 1200°C for 4 h and cooled slowly to room temperature in a purified N_2 atmosphere (annealed samples). Each sample was treated with HNO_3:HCl (1:3 v/v) solution for 60 s and finally cleaned with a concentrated HF solution at 50°C for 24 h. For the electrochemical deposition of Hg on foils, a degassed solution containing 60 mmol Hg_2^{2+} + 1 M KNO_3 + HNO_3 (pH 1) was used. The electrodeposition was performed by applying −0.46 V/ENH for 300 s in the stirred solution. These foils were washed several times by immersion in triply-distilled water, dried in a flux of N_2 and stored in a purified N_2 atmosphere.

TG curves were obtained at 5°C min^{-1}, under a flux of purified N_2 atmosphere (150 cm^3 min^{-1}) from 30 to 800°C (TG curves) using a Mettler Thermoanalyzer TA-4000 system.

The sample surfaces, before and after each had been heated to different temperatures, were examined by scanning electron microscopy (SEM) (JEOL JSM-T330A) and an energy dispersive X-ray microanalysis (EDX) system (NORAN).

For mercury analysis, blank solutions were prepared by treating pure Pt and Pt–Ir foils without Hg electrodeposition, with 1 ml of concentrated HNO_3 + 5 drops of concentrated HCl and 1 ml of concentrated HNO_3 + 3 ml of concentrated HCl in an ultrasonic bath, respectively; no Pt or Ir were detected in these solutions.

Solutions produced by the immersion of Pt and Pt–Ir alloy foils containing electrodeposited mercury, after treatments as described above, were made up to the required volume with tri-distilled water and a conserving solution [12]. Mercury was analysed by atomic absorption spectroscopy using the cold-vapor generation technique [13] in an INTRALAB-VARIAN, AA/1475 spectrometer, and Pt and Ir were analysed by ICP using an ICP-AES (Sequential Espectroflame) spectrometer.

3. Results and discussion

Fig. 1 shows the TG and DTG curves recorded on heating to >800°C for (a) annealed platinum, (b) annealed platinum–iridium alloy and (c) quenched platinum–

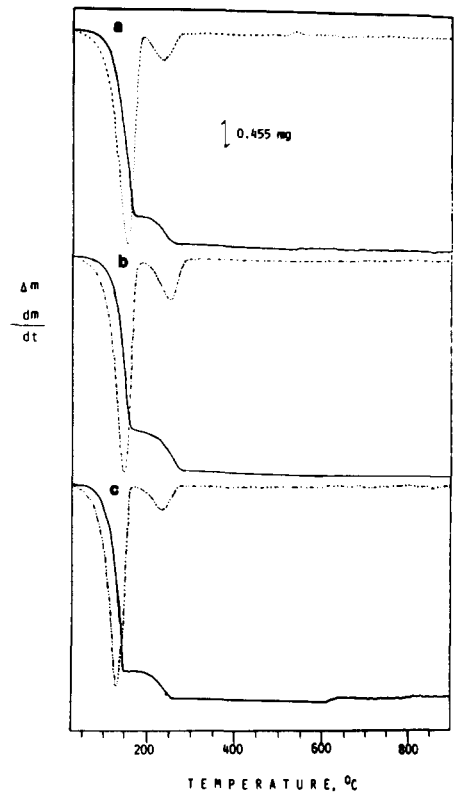

Fig. 1. TG (——) and DTG (···) curves for Pt and Pt–Ir foils containing electrodeposited Hg: heating rate, 5°C min^{-1}; N_2 flux (purified to remove traces of oxygen), 150 cm^3 min^{-1}; alumina crucible. Curve a, annealed Pt; curve b, annealed Pt–Ir alloy; and curve c, quenched Pt–Ir alloy.

iridium alloy. These curves show mass losses in three consecutive steps between 30 and approx. 600°C. The first mass loss occurred below 175°C (Fig. 1, curve a), 170°C (Fig. 1, curve b) and 145°C (Fig. 1, curve c) in a very fast process that can be ascribed to the loss of mercury electrodeposited on mercury (bulk mercury). The quantity of mercury lost in this step corresponds to approx. 85% of the total electrodeposited mercury, except for the annealed Pt–Ir alloy where the amount is only 80%. The resulting surface does not have a typically metallic surface because bulk mercury was eliminated. Considering pure platinum, these results and their interpretation are in agreement with the Refs. [9] and [10]; for the Pt–Ir alloy, these results do not agree with Ref. [3]. Figs. 2(a) and (b) show the SEM images of the surfaces of platinum and quenched platinum alloy after mercury electrodeposition and heating to temperatures corresponding to the end of the first step in the TG curves. These SEM images show the surface covered by a film and, in the case of Pt, the attack is mainly at the grain boundaries. The images reveal a considerable surface roughening.

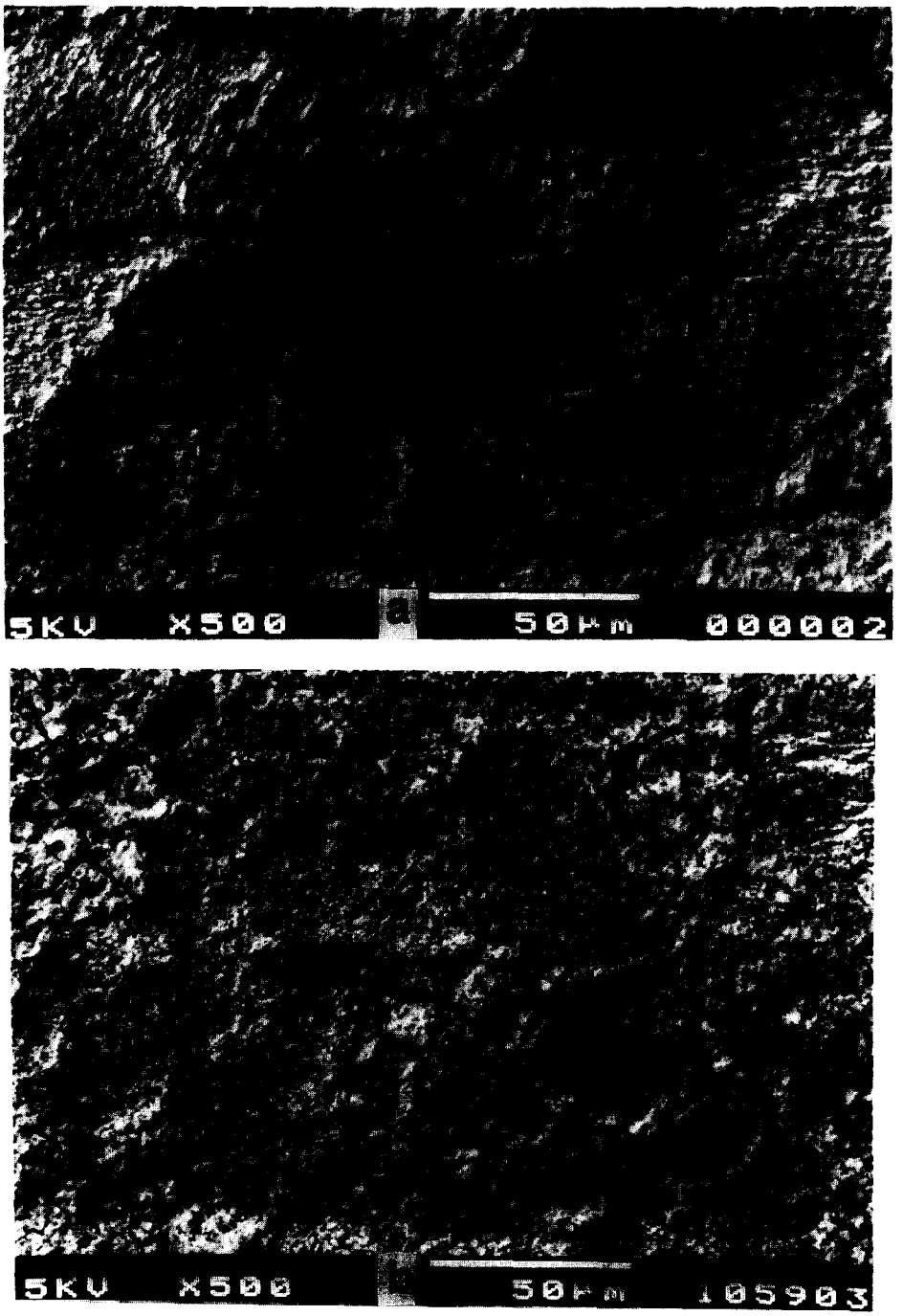

Fig. 2. SEM images of the surface of annealed platinum and quenched platinum–iridium alloy after mercury electrodeposition and heating to: (a) Pt, 170°C; (b) Pt–Ir, 145°C; (c) Pt, 260°C; and (d) Pt–Ir, 254°C.

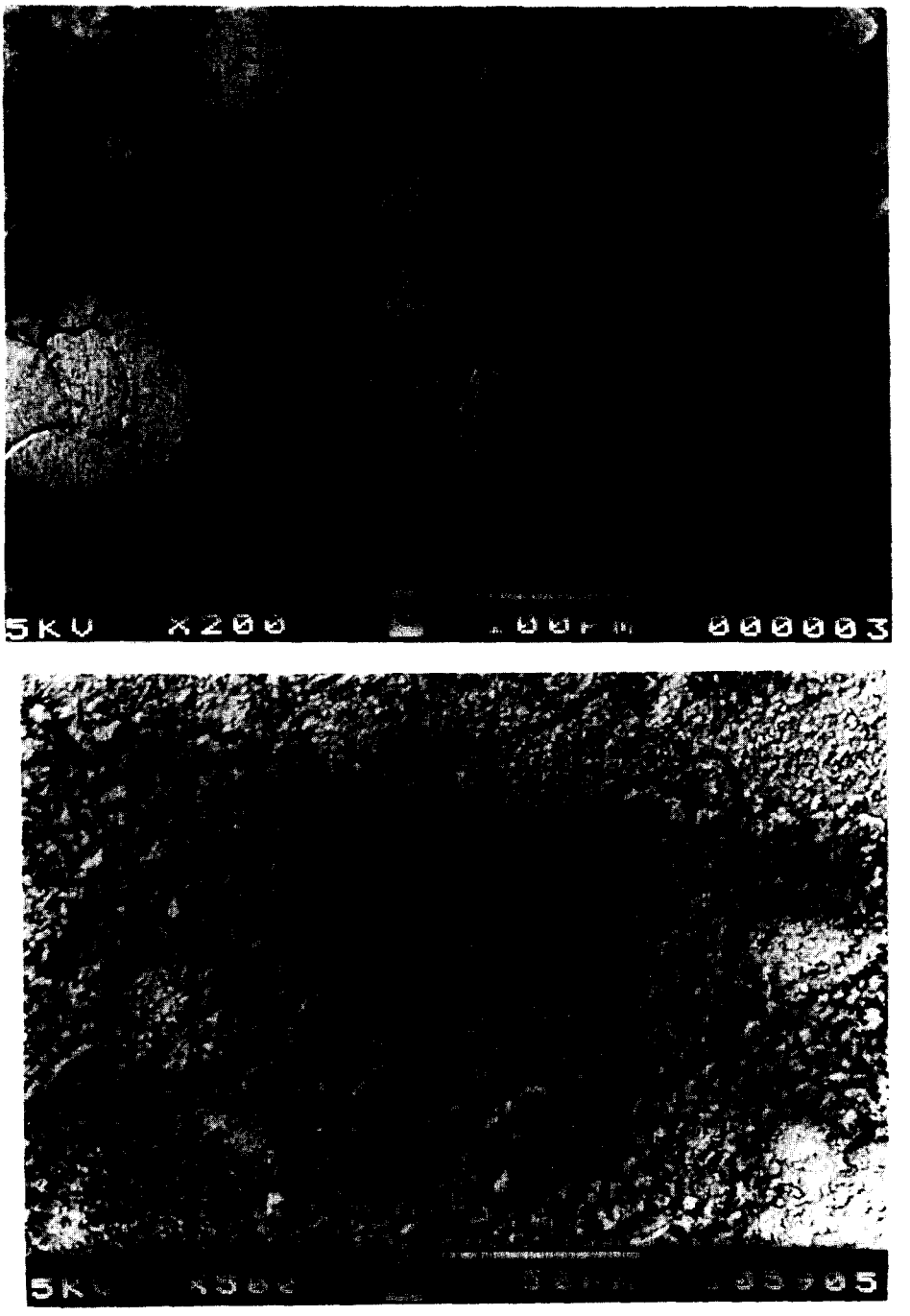

Fig. 2 *(Continued).*

Table 1
Flameless atomic absorption and atomic emission (AES-ICP) data for Hg, Pt and Ir after partial or total elimination of the mercury by heating to the specified temperatures

Material	T/°C	m_i/mg [a]	m(Hg)/mg	m(Pt)/mg	m(Ir)/mg
Pt–Ir (quenched)	170	27.378	0.956	0.0912	0.00458
	270	30.913	0.279	0.179	0.00873
	400	32.000	0.0229	0.141	0.00619
	800	26.629	0.00346	0.119	0.00669
Pt (annealed)	145	15.756	0.509	0.310	–
	280	17.263	0.0779	0.674	–
	350	17.638	0.0162	0.0979	–
	800	16.638	0*	0*	–

[a] m_i: total initial mass.
* Below the detection limit.

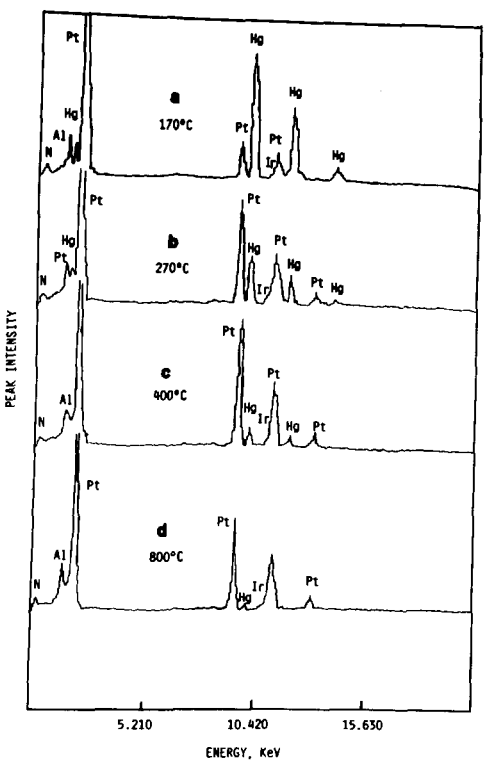

Fig. 3. EDX microanalysis of the surface of quenched Pt–Ir alloy at a sample time of 100 s: curve a, 170°C; curve b, 270°C; curve c, 400°C; and curve d, 800°C. Electron beam acceleration: 30 kV.

The second step observed between 175 and 260°C (Fig. 1, curve a), 170 and 280°C (Fig. 1, curve b), and 146 and 254°C (Fig. 1, curve c), which occurs as a fast process, can be ascribed to the elimination of mercury contained in a film, probably as $PtHg_4$ [11]. In this step, the mass loss was about 13% and 19% for pure platinum or the quenched platinum alloy and for the annealed platinum alloy, respectively. It is well known that Hg does not interact with Ir to form intermetallic species [3,14,15] and Pt–20%Ir alloy has been suggested as an appropriate substrate for mercury deposition because its surface is not scarred by interaction with mercury [3]. The presence of mercury on the platinum and platinum alloy surface in this temperature range was confirmed by means of EDX microanalysis (Figs. 3 and 4) and atomic absorption analysis (Table 1). For pure Pt and Pt–Ir alloy, the intensity of the Hg peaks diminishes as the heating temperature increases. In the case of pure Pt, no mecury peaks are observed when the sample was heated at 800°C, while they are still observed for the Pt–Ir alloy. For the atomic absorption analysis, the foils heated up to 170°C were treated as described in the experimental section. It is interesting to note that platinum and iridium were detected in this solution (Table 1), showing the surface instability caused by its interaction with

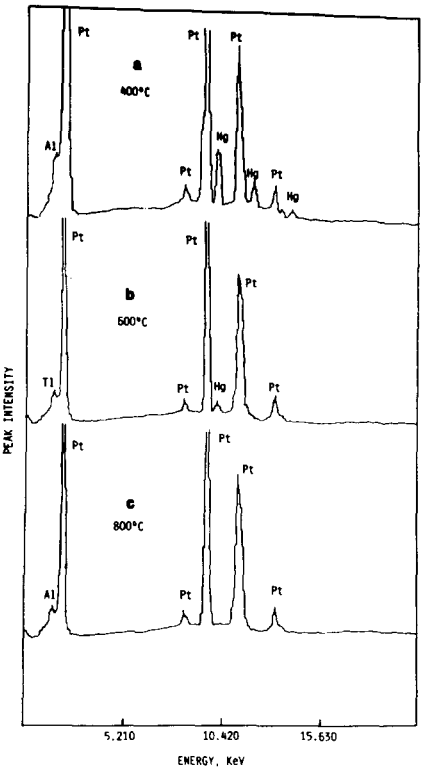

Fig. 4. EDX microanalysis of the surface of annealed platinum at a sample time of 300 s: curve a, 400°C; curve b, 600°C; and curve c, 800°C. Electron beam acceleration: 30 kV.

mercury. This seems to indicate that the atomic size factor between Hg and Pt and Ir may introduce a surface 'destructuration' which can facilitate the attack of the surface by the acid solution. Figs. 2c and d show the SEM images of the surfaces of platinum and quenched platinum alloy after mercury electrodeposition and heating to the temperature that corresponds to the end of the second step of the TG curves. The Pt surface shows grain boundaries which are not so clearly seen for the Pt–Ir alloy surface. It can be seen that the basic surface structure has been mantained when one compares Figs. 2a and b with 2c and d, suggesting that a film is still present on the surface. The Pt–Ir alloy exhibits a morphology that is very different from that shown by Pt.

The last step, which corresponds to a very slow process, can be attributed to the removal of mercury present as a solid solution (see Ref.[10] for pure platinum). For the pure platinum, continued loss of mercury is detected until approx. 500°C, and until approx. 600°C for the platinum alloy. In this step, the mass loss was approx. 1.7% for pure platinum and quenched platinum alloy and 1.2% for annealed platinum alloy. Mercury was also detected on the surface of the foils by EDX, even when the samples were heated at 600°C. After heating the samples to 800°C, only the quenched platinum alloy shows mercury on the surface, based on the EDX results. These results agree with those obtained using atomic absorption analysis (see Table 1).

Fig. 5 shows SEM images of the surfaces of platinum and of quenched platinum alloy after mercury electrodeposition and heating to 350°C (Figs. 5a and b) and up to 900°C

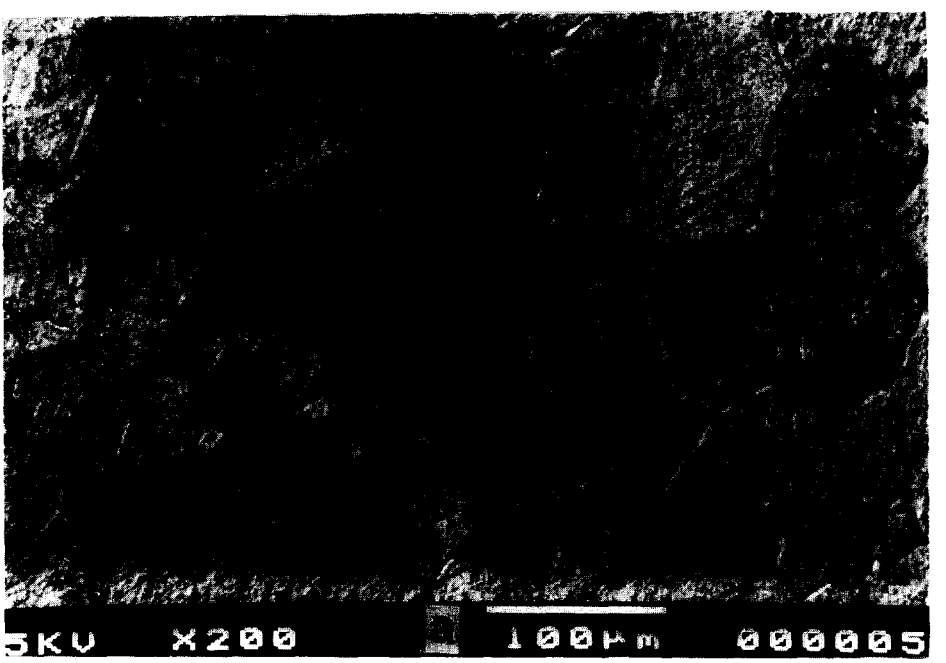

Fig. 5. SEM images of the surface of annealed platinum and quenched platinum–iridium alloy after mercury electrodeposition and heating to: (a) Pt, 350°C; (b) Pt–Ir, 400°C; (c) Pt, 900°C; and (d) Pt–Ir, 900°C.

Fig. 5 *(Continued).*

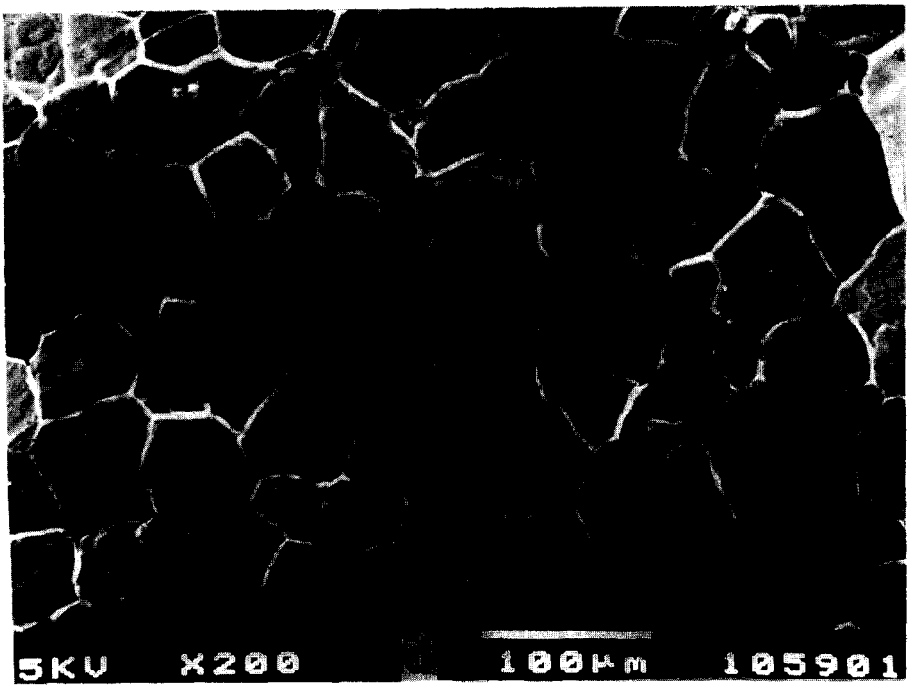

Fig. 5 *(Continued).*

(Figs. 5c and d) corresponding to the end of the last step in the TG curves. Figs. 5a and b, are similar to Figs. 2a and b, since the images correspond to surfaces heated up to approx. 350 or 400°C and up to 260 or 254°C, respectively, a range of temperatures in which no important changes are expected. Figs. 5c and d show surfaces cleaner than the others as a consequence of mercury elimination by heating.

4. Conclusion

The studies present here identify mercury film formation on Pt and a Pt–20%Ir alloy. This film can be formed by mercury electrodeposition on metal and metal alloy foils followed by heating to different temperatures. Mercury loss occurs in at least three steps: between the room temperature and 170°C, only the bulk Hg is removed; from this temperature to about 280°C, the mass loss can be attributed to the desorption of a monolayer of mercury; and finally, between 280 and $\approx$600°C, the mass loss step can be ascribed to the removal of Hg from solid solution in Pt or in the Pt–Ir alloy. EDX microanalyses have proved the presence of mercury on the metal and the metal alloy after heating to different temperatures, in agreement with the TG and DTG curves. SEM micrographs show that the grain boundaries are attacked under specified conditions and a clean surface could only be observed after samples had been heated to 900°C.

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