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Iridium–tin mixed oxide anode coatings

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Mixed oxide coatings of tin and iridium oxide on titanium substrates have been studied over the composition range of 5 to 100 mol % iridium oxide. While stannic oxide behaves as a simple diluent for the electrocatalytically active precious metal oxide, substantial replacement of iridium by tin may be made with little degradation of coating performance in oxygen evolution.

1. Introduction

In recent years there has been increasing interest in titanium metal anodes activated with iridium oxide-based coatings. A major technological advantage of a coating based on this metal over the more common ruthenium–titanium mixed oxide coating is its ability to evolve oxygen in strongly acidic environments while maintaining good catalytic activity and dimensional stability. High current density water electrolysis [1] and high speed electrogalvanizing of steel [2] are two recent applications which require such increased durability. Iridium oxide-based anode coatings have been discussed in a recent review [3].

A large literature exists on the preparation and properties of mixed coatings of ruthenium oxide with refractory metals [3–7] and mixed iridium oxide–ruthenium oxides have been described [8–10]; considerably less information is available on the behavior of other iridium-containing mixed oxide coatings.

Rolewicz and his coworkers have described the preparation and behavior of iridium oxide–tantalum oxide coatings [11, 12]. This pair of oxides is not miscible to any significant extent and separate metal oxide phases were noted in the X-ray diffraction patterns. There was, however, a promotional effect, with a maximum in anode service life noted at 70 wt % tantalum. Noguchi *et al.* [13] have similarly reported the addition of cobalt oxide to iridium oxide coatings to result in an increase in durability. Matsumoto and his collaborators produced an iridium oxide–titanium oxide mixed coating by vigorous anodization of the titanium substrate prior to application of the iridium chloride coating mixture; increased catalytic activity and durability were found [14].

Stannic oxide adopts the rutile crystal structure [15] and solid solution ruthenium–tin oxide coatings are well known [16–18]. Hutchings, Muller, and Stucki [19] in a study of powder compact electrodes, rather than coatings on titanium, prepared a solid solution of tin, iridium, and ruthenium oxides and found the base metal oxide to promote the catalytic activity of the mixture. Iwakura *et al.* have described a ternary tin–antimony–iridium oxide coating containing 5 mol % of the precious metal and its behaviour in unit molar potassium hydroxide solution [20]. In this report, we describe binary iridium–tin oxide coatings containing from 5 to 100% precious metal and the anodic behaviour of these compositions in strongly acidic solutions.

2. Experimental details

The titanium substrates were in the form of plates, 1.6 mm in thickness, which had been etched in oxalic acid. The coating mixture was a solution of the iridium (III) and stannous chlorides in butanol at the appropriate molar ratio; multiple applications and firing at 400° C was used to build a coating thickness of $15\,\mathrm{g\,m^{-2}}$. All concentrations are expressed as mol %.

Electrochemical measurements were made in a thermostatted, three compartment cell of conventional design using a PAR Model 173 Potentiostat and Model 175 programmer. Nitrogen was bubbled through the electrolyte during cyclic voltammetry scans while oxygen was used during polarization measurements. Potential-pH dependence data were measured using a pH meter in the millivolt mode.

Coating life testing was carried out in simple undivided glass cells with a two molar sulphuric acid (reagent grade) electrolyte thermostatted at 70° C. A constant $775\,\mathrm{mA\,cm^{-2}}$ current density was used; cell voltage under these conditions was normally approximately 3.5 V. Two separate series of tests were run. The end of useful service life was taken to be the time at which the cell voltage had tripled. As was the case with the materials in this study, the onset of passivation of coated anodes under such accelerated conditions is normally sudden and the voltage increase rapid.

Auger analyses and depth profiling of the oxide films were carried out on the anodes which had been used earlier for electrochemical measurements. Sputtering depths are relative to silica. The Auger measurements were made by Richard L. Moore of the Physical Electronics Laboratory, Metuchen, New Jersey.

3. Results and discussion

3.1. *Coating characterization*

Scanning electron microscopy revealed a substantial change in surface texture with metals ratio. At high

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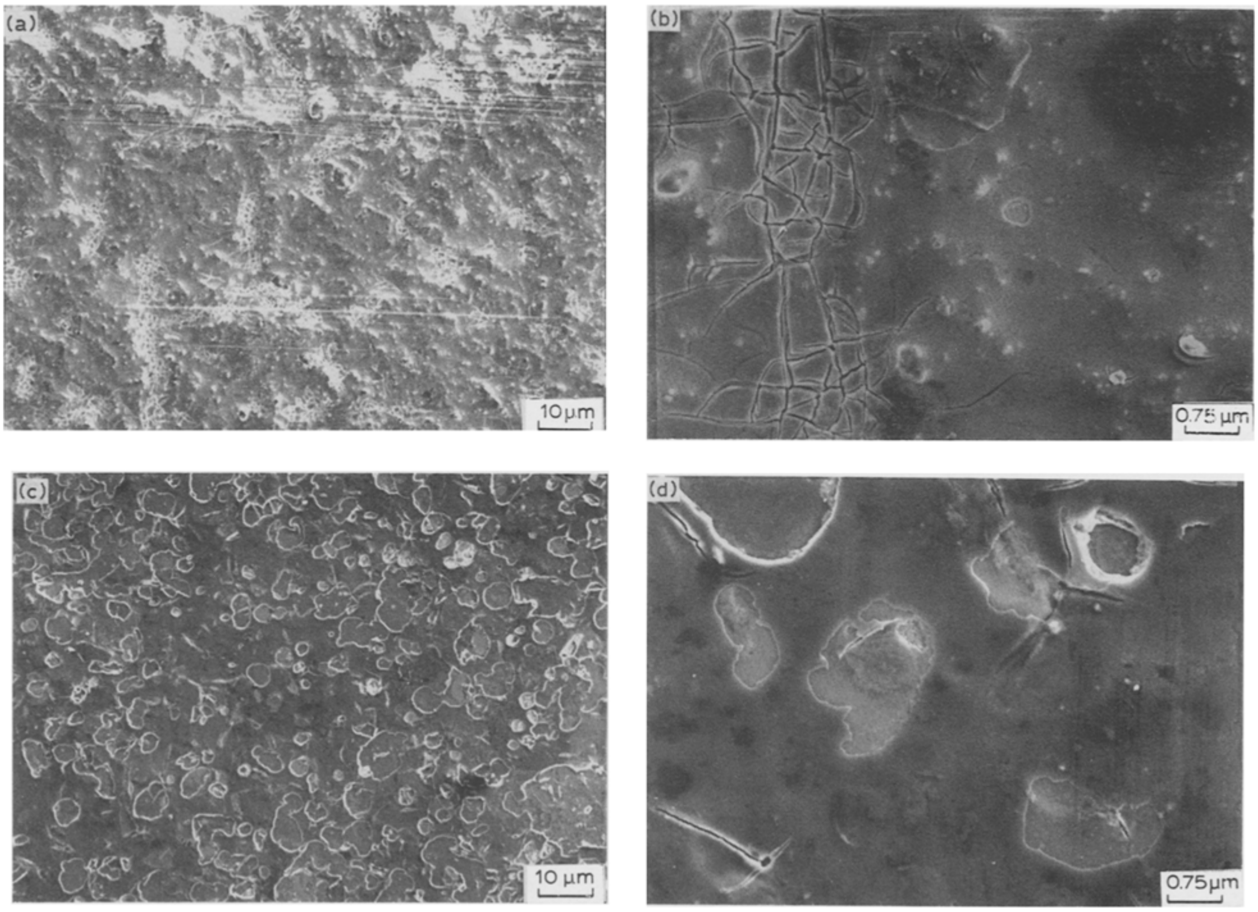

Fig. 1. SEM plates of (a) and (b) the 50Ir/50Sn film (same field) and (c) and (d) the 10Ir/90Sn film (same field).

precious metal content, the coatings contained many regions with the "mud-cracked" morphology well-known for thermal anode coatings [21]. As the tin content is increased, the surface becomes less rough, ultimately achieving a glazed appearance evident at the 10Ir/90Sn ratio. Figure 1 presents SEM photographs of the 50Ir/50Sn film, a coating with a substantial proportion of cracked regions and of the 10Ir/90Sn film in which the glazed texture is clearly evident.

A composition versus depth profile for the 20Ir/80Sn film is presented in Fig. 2. From the profile it is evident that the coatings of this study had, in fact, three metal ion components; tin and iridium from the coating mixture and titanium which was contributed by the substrate. In general, the concentration of tin or iridium at the surface was somewhat different from the bulk; Table 1 compares surface concentrations to those measured at depths of one-half and one micron. The differences were not systematic with both surface enrichment and surface depletion of both metals occurring within the series. Chlorine was present at a level of several percent throughout the coating; this is well known in films prepared by pyrolysis of that halide [3].

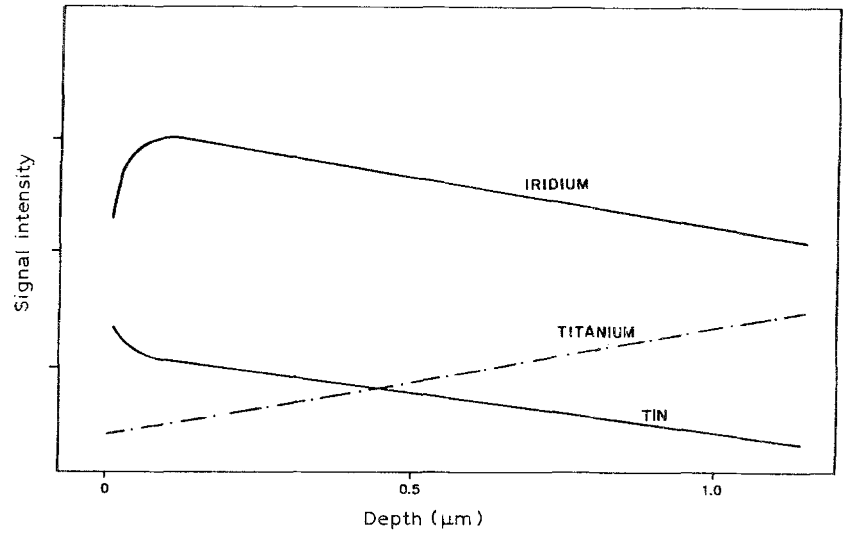

Fig. 2. Concentration profile of tin, iridium and titanium in the 20Ir/80Sn coating. The etching rate was 20 nm min^{-1}.

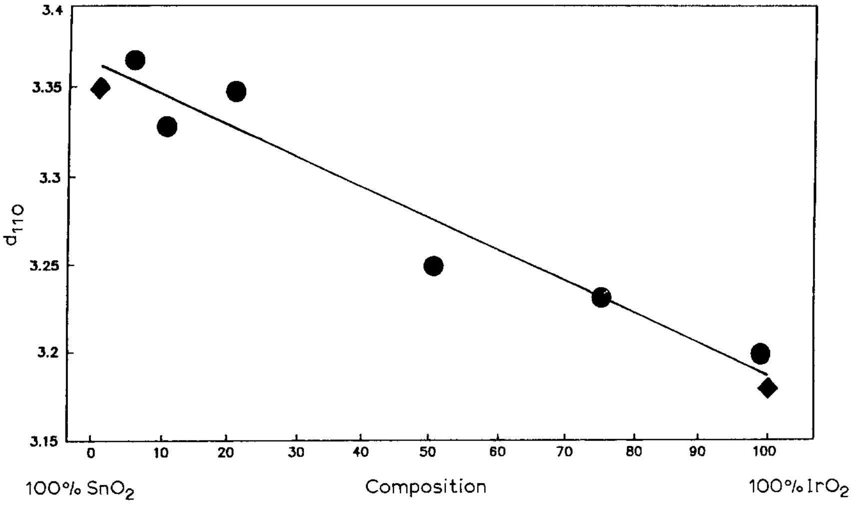

Fig. 3. Variation of d_{110} of the films as a function of iridium content. The circles represent measurements made in this work, the diamonds are literature values from the JCPDS file.

X-ray diffraction measurements found only a single rutile phase to be present throughout the entire composition range. The smooth variation in the d_{110} parameter with composition measured for these films is shown in Fig. 3.

3.2. *Cyclic voltammetry*

Following pH-potential measurements, cyclic voltammetry was done with the same new coating samples in unit molar sulphuric acid at 20° C. There were only small differences between the first and subsequent scans and by the fifth cycle, the recorder traces had ceased to change; these invariant scans are collected in Fig. 4.

There are several differences evident in the behaviour of the various compositions. The voltammetric charge passed as the samples were cycled exhibited a minimum in the material which contained 20% iridium then increased with either tin or iridium content. This is evident in Fig. 4 where the end members of composition series have traces nearly equal in magnitude while intermediate metal ratios exhibit lower values of charge.

A second difference is evident in the region above 1000 mV in the positive-going scan. The magnitude of the current there is greatest for the pure iridium oxide coating and decreases with iridium content. Bulk iridium oxide is known to undergo a redox process in this region [22] and it is likely that the variation in current with composition merely reflects the differing quantity of iridium available to take part in the reaction.

3.3. *Polarization behaviour*

Figure 5 presents polarization curves for the different compositions in unit molar sulphuric acid, under flowing oxygen, at 30° C. As is apparent from the low polarizations, particularly with the iridium-rich coatings, these are materials of high electrocatalytic activity. Table 2 collects Tafel slope data at an applied geometric current density of 400 mA cm^{-2} and, as a measure of catalytic activity, electrode potential against SCE at the same current density.

The measurement for the pure iridium oxide coating is in agreement with the literature where values from 56 to 90 mV decade^{-1} have been reported for that single component coating in strongly acidic solution [10, 14, 23, 24]. There is no evidence of an enhancement of electrocatalytic activity by tin oxide; polarization of the 75Ir/25Sn coating was the same as that for the pure precious metal oxide while greater tin contents caused polarization to increase.

The change in polarization behaviour with composition is quite small for rather substantial levels of

*Table 1. Metal concentration as a function of depth**

Film bulk composition	*Tin*		*Iridium*	
	$C_s/C_{0.5}$	C_s/C_l	$C_s/C_{0.5}$	C_s/C_l
Pure IrO_2	–	–	1.0	1.4
75Ir/25Sn	1.6	1.9	0.7	0.7
50Ir/50Sn	0.2	0.2	1.4	1.4
20Ir/80Sn	1.3	3.0	0.9	1.0
10Ir/90Sn	1.1	1.1	0.7	0.7
5Ir/95Sn	0.9	1.0	0.9	0.7

* C_s, $C_{0.5}$, and C_l are the concentrations of the metal, as manifested by the peak-to-peak height of the Auger signal, at the film surface and at depths of one-half micron, and one micron, respectively.

Table 2. Polarization data in 1 M sulphuric acid at 30° C

Composition	*Tafel Slope (mV decade^{-1})*	*Polarization at 400 mA cm^{-2} (mV/SCE)*
Pure IrO_2	70	1290
75Ir/25Sn	70	1290
50Ir/50Sn	70	1310
20Ir/80Sn	100	1340
10Ir/90Sn	140	1360
5Ir/95Sn	170	1400

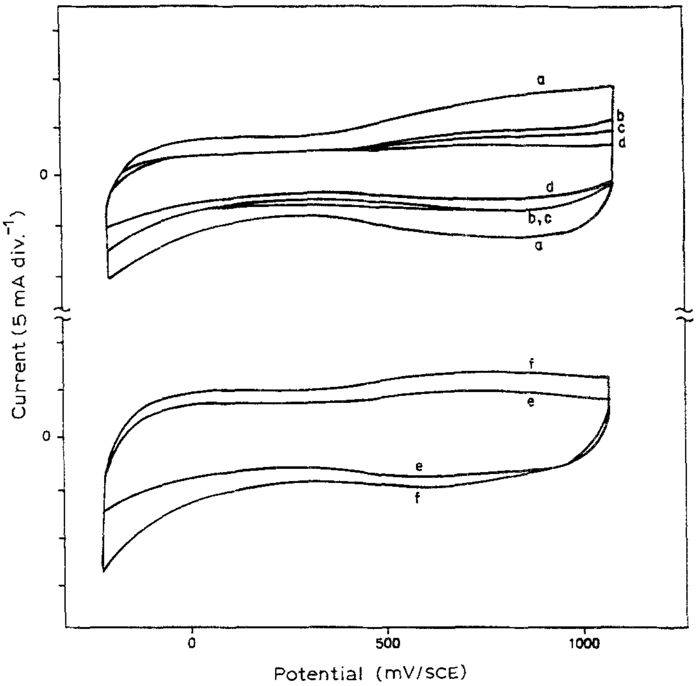

Fig. 4. Cyclic voltammograms of the various film compositions. Scan rate: 20 mV s^{-1}. Key: (a) 100Ir, (b) 75Ir/25Sn, (c) 50Ir/50Sn, (d) 20Ir/80Sn, (e) 10Ir/90Sn and (f) 5Ir/95Sn.

substitution of iridium by tin; the largest change occurs when the iridium content is decreased from 20 to 10 mol %. The significant increase in polarization and the Tafel slopes in excess of 2*RT*/*F* suggest a transition to semiconductor behaviour in the high tin content materials. The ruthenium oxide–tin oxide system is reported to exhibit similar behavior in chlorine evolution but in that case, the transition occurs at a greater level of substitution, at approximately 94 mol % tin [25].

3.4. *Potential-pH behaviour*

The open-circuit potential pH behaviour was identical for all samples prepared in this study over the range examined, pH 4 to pH 10. Figure 6 illustrates the data obtained for the end members and centre point of the composition range after sixty minute equilibration with each buffer solution. The slope, 66 mV decade^{-1} of hydrogen ion activity, is in reasonable agreement with the 59 to 64 mV decade^{-1} range reported for pure iridium oxide [26, 27].

3.5. *Coating durability*

The results of the accelerated testing of coating durability are presented in Fig. 7. The results were remarkably consistent for anode coating testing of this type. There was little difference in the time-to-failure of compositions which contained more than 20% iridium oxide. The general trend in the other electrochemical measurements of a discontinuity in behaviour below 20 mol % precious metal oxide is reflected here as well.

4. Conclusions

When calcined on the surface of a metallic titanium substrate, iridium and tin chloride pyrolyze to form a

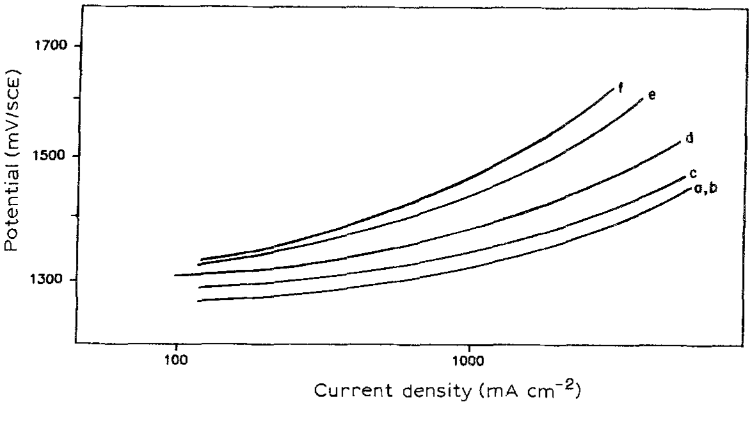

Fig. 5. Polarization curves in unit molar sulphuric acid at 30°C. Scan rate: 2 mV s^{-1}. Key: (a) 100Ir, (b) 75Ir/25Sn, (c) 50Ir/50Sn, (d) 20Ir/80Sn, (e) 10Ir/90Sn and (f) 5Ir/95Sn.

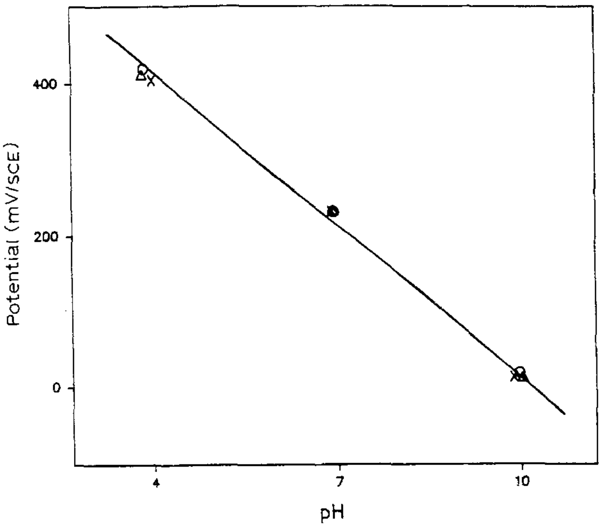

Fig. 6. Potential of several of the film compositions against SCE as a function of pH. Key: (O) 100Ir, (x) 50Ir/50Sn and (△) 5Ir/95Sn.

series of solid solutions over the composition range of 5 to 100 mol % iridium oxide. Quite extensive substitution of iridium by tin may be made with little change evident in polarization behaviour. All compositions were indistinguishable from the pure noble metal oxide in the behavior of open-circuit potential as a function of solution pH. A discontinuity in other electrochemical behaviour of the mixed oxides occurs at iridium oxide contents of lower than 20%; at that point polarization increases and coating durability is degraded.

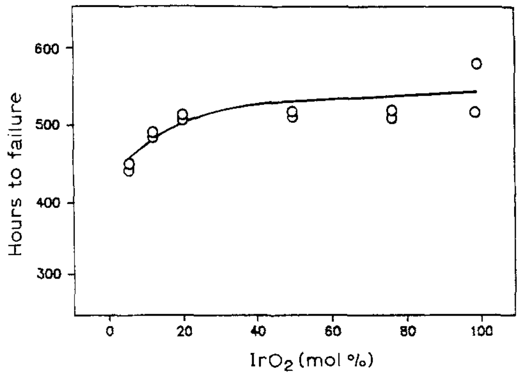

Fig. 7. Results of accelerated endurance testing.

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