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STRUCTURAL PROPERTIES OF Ru-Ti-Sn MIXED OXIDE COATINGS

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The structural effect on the addition of tin oxide to RuO_2-TiO_2 mixed oxide coatings has been presented. X-ray diffraction patterns indicate a highly complex structure above 20% SnO_2 in the ternary mixture. Considerable deviations in the RuO_2-TiO_2 structure do not occur below this limit. The electrical conductivity shows a linear dependence on the SnO_2 content. The morphology of the films changes from cracked-mud appearance to compact surface as the SnO_2 increases. Higher overpotentials shown by electrodes having Ru:Sn ratio in the range of 1.5 to 3.0 have been attributed to the presence of Sn atoms at the surface. Lower crystallinity at higher SnO_2 contents indicates a high surface area that may be responsible for their enhanced oxygen evolution.

Key words: Ru-Ti-Sn mixed oxide electrode, X-ray diffraction, conductivity

INTRODUCTION

The ruthenium oxide based electrodes have found applications in many of the industrial electrochemical processes [1]. Their high catalytic activity for chlorine and oxygen evolution is well known [2], but the lack of stability of these electrodes under oxygen evolution conditions is still a matter of active investigation [3-5]. Additives, such as Ta_2O_5[5], IrO_2[6], ZrO_2[7], SnO_2[1] etc., have been suggested for the stabilisation of RuO_2 during oxygen evolution. Of these, the inclusion of SnO_2 has much preference in view of its cost effectiveness in the commercial electrodes.

The electrocatalysis of doped-SnO_2 electrodes [8- 13] and the effect of composition on the life of RuO_2- SnO_2 electrodes [14] have been reported. Mixed oxide containing tin to partly replace ruthenium was given in an earlier patent [15]. But the basic criteria of the inclusion of SnO_2 and the mechanism of its stabilising action are not clear. The objectives of the present investigation are to determine the structural changes occurring in RuO_2-TiO_2 due to the addition of SnO_2. In this work the RuO_2 content of the ternary mixtures is maintained at 30 mol% and the TiO_2 and SnO_2 contents are varied.

EXPERIMENTAL

The mixed oxide electrodes were prepared by the thermal decomposition process as described in the literature [16]. The chloride of ruthenium, titanium and tin were dissolved in isopropanol to give the required composition of the final coating. The titanium strips (4 x 1 x 0.1 cm) were polished, degreased and etched in 10% oxalic acid solution at 363K for 30 mts. The coating solution was painted on to the surfaces, dried at 373K and heated in air at 673K for 5mts. This process was repeated ten times and the final heating was carried out at 723K for one hour. The amount of oxide (2-2.5 mg.cm^{-2}) formed on the titanium strips was estimated by weighing. For resistivity measurements silica pieces (2x2 cm) were degreased and coated with the oxides as above.

X-ray diffraction studies were made using a Philips vertical powder diffractometer (PW 1050) with a Philips X-ray generator (PW 1130) and a proportional counter. The scanning rate was 1° per minute.

The resistivity of the coatings on silica was measured using the four- probe technique. The polarization measurements were made using a Wenking-HP 72 potentiostat and an external ohmic resistor, in the usual H-type cell.

RESULTS AND DISCUSSION

X-ray diffraction studies

The microstructural investigation was carried out by examining the diffractograms of electrodes containing 30 mol % Ru with varied amounts of Ti and Sn. Fig. 1 shows the diffraction patterns of the mixed oxides containing 20, 40, and 70 mol % of tin. The diffraction angles (2θ) of all the three major peaks continuously shift towards lower values as the SnO_2 content increases. All the three peaks broaden with increasing SnO_2 the maximum being at 40 mol % Similarly the height of the peaks shows a minimum in the same range. The base of the peaks is skewed towards lower angles at and below 20 mol %.

In the diffraction patterns, the peaks corresponding to SnO_2 were not identified even when it is present in larger proportions. This is in line with the observation [13] that the SnO_2 crystal structure is destructed even at 5% doping of RuO_2. The splitting and broadening of the peaks as the tin oxide content increases, indicates a complex structure of the coating rather than miscibility. Because of the identical crystallographic features (Table I) [17] the formation of solid solution is expected.

TABLE-I: Crystallographic properties of RuO_2, TiO_2 and SnO_2

Property	RuO_2	TiO_2	SnO_2
Space group	D_{4h}^{14} P $\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$	D_{4h}^{14} P $\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$	D_{4h}^{14} P $\frac{4_2}{m}\frac{2_1}{n}\frac{2}{m}$
Crystal structure	Rutile	Rutile	Rutile
Crystal habit	Tetragonal	Tetragonal	Tetragonal
Lattice constants (nm)			
a	0.4519	0.4594	0.4737
c	0.3116	0.2958	0.3185
c/a	0.68	0.644	0.673

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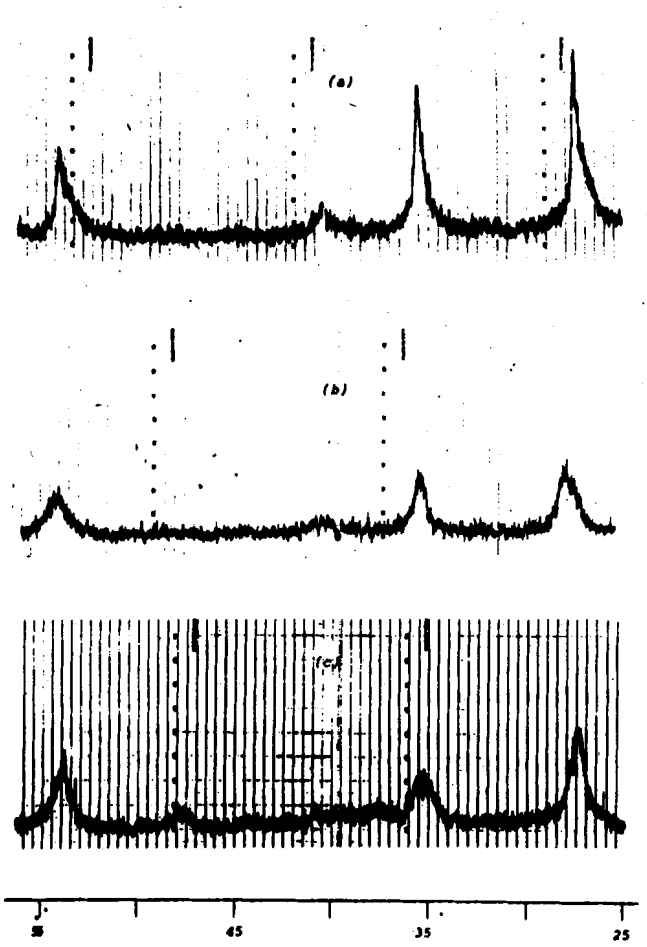

Fig. 1: X-ray diffraction patterns of the mixed oxide coatings: (a) RuO_2 (30) TiO_2(50) SnO_2(20), (b) RuO_2(30) TiO_2(30) SnO_2(40), (c) RuO_2 (30) SnO_2 (70)

But even in the case of the binary mixture, RuO_2-TiO_2, the earlier view [18,19] of solid solution formation has been contradicted [20]. Further, only limited solubility has been reported [16] for IrO_2-TiO_2 and IrO_2-SnO_2 systems. The skewing of the peak bases at lower tin oxide contents suggests the inclusion of Sn atoms in the RuO_2-TiO_2 structure. Similar effect has been observed [5] in the case of RuO_2-Ta_2O_5 electrodes. When the ratio of Ru:Sn decreases below unity (> 20%), it is probable that the SnO_2, not included in the Ru/Ru-Ti oxide crystallites is present as Cl or Ru doped species. All these components must exist as a finely dispersed separate phase as suggested [20] for Ru-Ti mixed oxide.

From the observed 2θ values the d-spacings have been calculated. The d-spacings increase linearly with tin oxide content and a change of slope has been observed between 20-30 mol%. The variation for (110) peak is shown in Fig. 2 and the other two peaks behave similarly. This is in support of the fact that the possibility of solid solution formation is rather less.

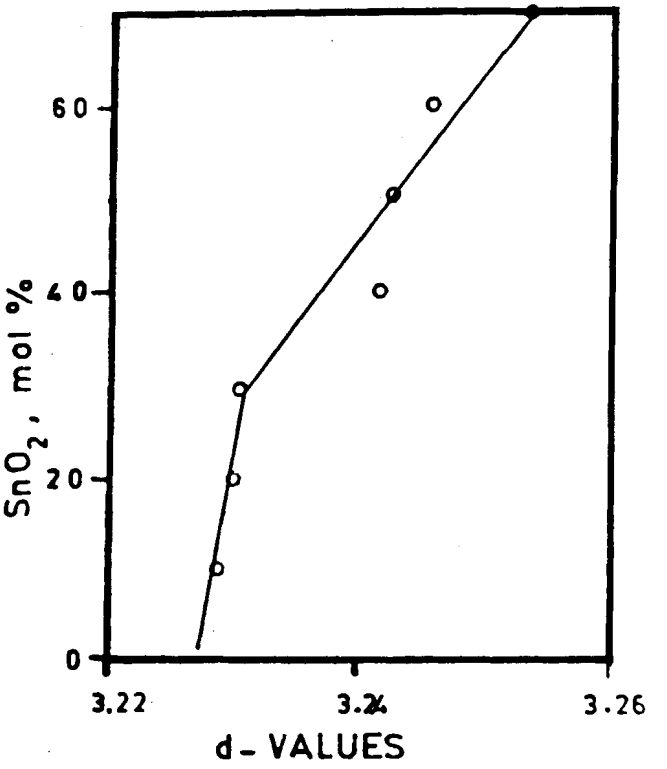

Fig. 2: Variation of the d-spacings of the (110) peak with SnO_2 content

The crystallite sizes calculated from the half-width of the (110) peaks were 20 nm for compositions with less than 20 mol% SnO_2 decreasing to 10 nm as the addition increases. This may be due to microcrystallinity only because the (110) peak of SnO_2 itself has been found [13] to be broad even in the absence of RuO_2, indicating the amorphousness of SnO_2.

The lattice constants 'a' and 'c' calculated from (110) and (211) peaks show a slight increase (about 0.8% and 0.18% respectively) compared to RuO_2-TiO_2 (30/70). This may be interpreted, on the basis of higher values of 'a' and 'c' for SnO_2, that a finite inclusion of tin oxide occurs in the RuO_2 lattice. The observations presented here are in agreement with the earlier report [13] on RuO_2-SnO_2.

Electrical conductivity

Fig.3 shows the linear increase of conductivity with SnO_2 content. The data given cannot be taken for absolute values, but the figure shows the relative change in the conductivity of the films as tin oxide was added. The enhancement of conductivity of the noble-metal doped SnO_2 over pure SnO_2 has been reported earlier [11,13]. The increase in conductivity with more addition of tin oxide must result from the progressive replacement of the nonconducting TiO_2 phase by the doped SnO_2.

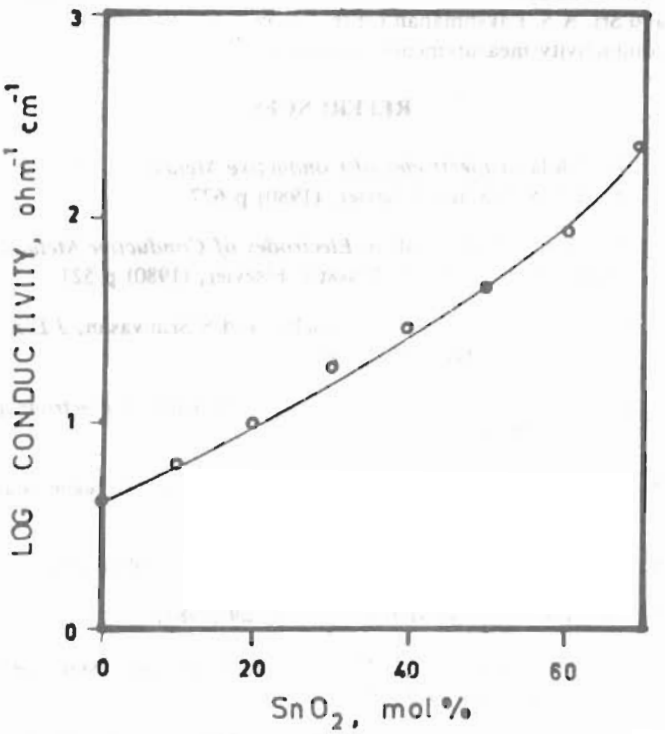

Fig. 3: Effect of composition on the electrical conductivity of the oxide films

Surface examination

SEM micrographs of various oxide surfaces are shown in Fig.4.

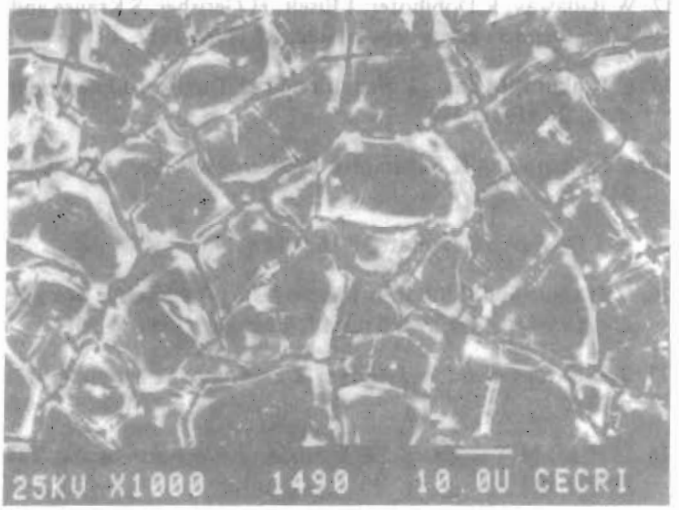

Fig.4 (A)
SEM photograph of the oxide surfaces: RuO_2 (30) TiO_2(50) SnO_2(20)

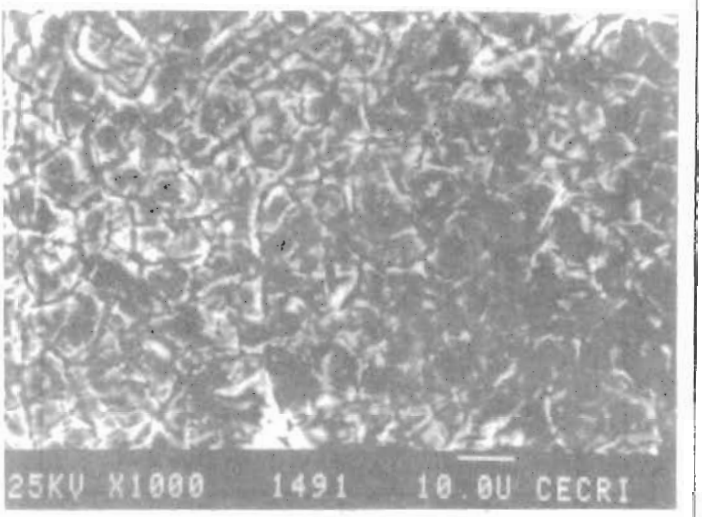

Fig.4 (B)
SEM photograph of the oxide surfaces: RuO_2 (30) TiO_2(30) SnO_2(40)

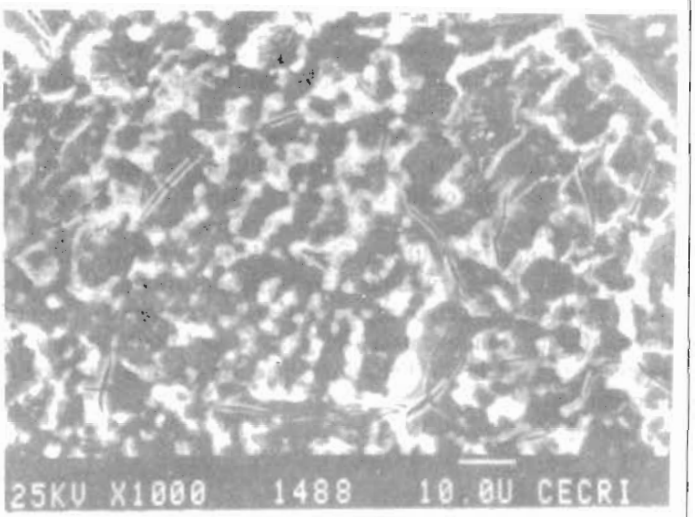

Fig.4 (C)
SEM photograph of the oxide surfaces: RuO_2 (30) SnO_2(70)

The usual mudcracked appearance of the RuO_2-TiO_2 gradually disappears as tin-oxide content increases. The number of cracks and pores diminish with the surface becoming smooth and compact. As mentioned above, the lower crystallite sizes and amorphous nature of the SnO_2 must be responsible for this change in the morphology of the surface. The compactness must also be one of the reasons for the observed increase in the conductivity.

Polarization studies

Fig. 5 gives the anodic polarization curves of the mixed oxide electrodes in 1N sulphuric acid.

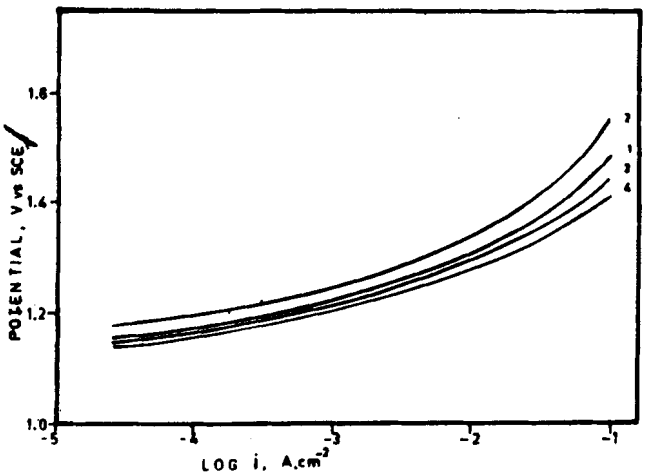

Fig. 5: Polarization curves of the mixed oxide electrodes in 1N H_2SO_4: (1) RuO_2(30) TiO_2(70), (2) RuO_2(30) TiO_2(50) SnO_2(20), (3) RuO_2(30) TiO_2(30) SnO_2(40) and (4) RuO_2(30) SnO_2(70)

The potentials were higher for electrodes having less than 20 mol% tin oxide and lower for those with larger contents. The Sn atoms included in the initial stages of SnO_2 addition, as predicted from x- ray patterns, must also be present at the surface replacing some of the Ru species. It has already been pointed out [14] that oxygen evolution occurs only at noble-metal sites in the case of doped-SnO_2 films. Because of the occupation of the Ru sites by Sn, the number of active centers are less causing the potentials to raise. The decreasing potentials with increasing addition of SnO_2 must be related to the lower crystallite sizes, microporosity and conductivity. Data on the surface area and the relative concentrations of the individual components at the surface and the bulk may be necessary to explain this behaviour. The work in this direction is in progress.

CONCLUSION

The x-ray analysis of tin oxide containing RuO_2-TiO_2 indicates microcrystallinity and a complex crystal structure of the coatings in which Ru:Sn ratios are below 1.5, whereas above this limit the effect is only marginal. Inclusion of tin atoms, to a limited extent, into the RuO_2 crystallite is inferred from the characteristics of the diffraction peaks. The observed increase in the electrical conductivity of the films with increasing tin oxide is attributed to the close packing and even distribution of doped- SnO_2 within the matrix. The change in the surface morphology supports this view. The polarization behaviour is also corroborative of the above conclusions and suggests a possible relationship between the physical and electrical properties of the mixed oxide.

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