JOURNAL OF APPLIED ELECTROCHEMISTRY 8 (1978) 417–425

Microstructural investigations on mixed RuO_2-TiO_2 coatings

W. A. GERRARD*, B. C. H. STEELE

Department of Metallurgy and Materials Science, Imperial College, London, UK

Received 12 October 1977

Mixed oxide coatings consisting of varying proportions of RuO_2 and TiO_2 have been prepared on titanium and silica substrates. Development of the microstructure was examined by X-ray diffraction and also monitored by resistivity measurements. The X-ray results suggest that the mixed oxide coatings prepared at 400° C are best described as a metastable solid solution of the two components. The resistivity–composition relationship however is more indicative of a finely interdispersed mixture of conducting and insulating particles. Coatings fired at higher temperatures (700–800° C) exhibit separate X-ray diffraction peaks corresponding to almost pure RuO_2 and TiO_2 phases with no evidence of significant solid solubility.

---

1. Introduction

Oxide-coated titanium anodes are now finding widespread application in the chlor-alkali industry [1]. Many investigations on the electrochemical properties of pure RuO_2 and RuO_2–TiO_2 coatings have now been described in the literature [2–8] but relatively few details have been published about the microstructural properties of these oxide coatings. Pizzini *et al.* [9] described some of the microstructural features of pure RuO_2 coatings, whereas O'Leary and Navin briefly reported [10] on the properties of a coating having the composition ratio $TiO_2 : RuO_2$ of 2:1. More recently Hine *et al.* [11] have published the results of a more extensive structural investigation into a series of TiO_2–RuO_2 coatings.

It is recognized that changes in the conditions of preparation of the TiO_2–RuO_2 coatings can produce significant changes in the electrochemical behaviour, and it was appropriate, therefore, in the present investigation to investigate the development of microstructure and its possible influence upon the electrochemical properties. It was also important to examine whether information about the defect solid-state chemistry of rutile-type oxides [12, 13] had any relevance to the electrocatalytic properties of RuO_2–TiO_2 coatings as it has been demonstrated that crystallographic shear planes can influence the electrochemical behaviour of Mo_4O_{11} [14].

The resistivity of the oxide coatings was also measured to provide additional information about the development of the microstructure.

2. Experimental procedure

The microstructural investigations were made on RuO_2–TiO_2 coatings prepared on either flat titanium or silica substrates. Sections of titanium sheet (1 in × 1 in × 1/16 in) were degreased with acetone and then etched in boiling HCl (109° C) for 30 minutes. Patent literature has stressed the importance of a good keying surface and the etching time was chosen after SEM investigations [15]. The silica substrates were optical flats which were also degreased prior to application of the oxide coatings. Preliminary experiments with a variety of reagents and procedures indicated that the most stable and homogeneous coatings were prepared from 0·4 M solutions of $RuCl_3 \cdot xH_2O$ (Johnson Matthey; Ru = 40·4 wt%) and $TiCl_4$ (Hopkins and Williams) in isopropanol mixed to give the required Ru/Ti ratio in the fired coating. The mixed

---

* Present address: Materials and Energy Research Centre, Aryamehr University of Technology, PO Box 41-2927, Tehran, Iran.

chloride solution was applied to the substrate with a pencil brush, and the solvent allowed to evaporate before introducing the sample into a well-ventilated furnace mantained at 400° C for five minutes. This coating procedure was repeated until the desired coating thickness was obtained. Five to six applications resulted in a coating thickness of about 2 μm. After the final application, the coatings were usually annealed for a further 6 hours except in those experiments where the development of microstructure was being investigated and which required a variety of annealing periods.

All X-ray diffraction measurements were made on a Philips vertical powder diffractometer employing a PW 1050/25 goniometer, copper target supplied by a PW 1310 generator, and a xenon-filled proportional counter (PW 1965/20). A McLean curved graphite crystal monochromator was included for accurate step-scan determinations. An annealed gold-coated optical slide was used as a standard.

The resistivity measurements were carried out on oxide coatings applied to sections of silica tube as the substrate material. Shallow grooves located close to the ends of each tube, were used to position platinum wires employed as the electrical connections. The coatings were applied to the silica substrate as described above, taking care to make good contact with the platinum wires. Initially a four-point probe method was used but as all contacts were found to be ohmic with negligible contact resistance the simpler two-point probe technique was subsequently used in most of the experiments. A Solartron 704 digital multimeter was employed to measure the resistivities. To monitor the change in resistivity with time during annealing a constant-current source was applied to the two platinum contact wires and the resulting potential followed on a Servoscribe recorder.

3. Microstructural characterization and discussion

Accurate values for the lattice parameters of rutile TiO_2 are available [16], whereas there is some disagreement over the precise values of a_0 and c_0 for RuO_2 [16–19]. As the difference in lattice parameters of RuO_2 and TiO_2 is small it was essential to check the data for RuO_2 using the same equipment employed to investigate the RuO_2–TiO_2 coatings. Accordingly, small crystals of RuO_2 were crushed and examined by X-ray diffraction using slow scans of the major peaks. The derived values for the lattice parameters are reported in Table 1 and can be seen to be in good agreement with available values from the literature.

The series of oxide coatings on flat titanium sheets was next examined by fast-scan (1° min^{-1}) X-ray diffraction. The composition of the painted coatings fired at 400° C varied from 0–100 mol% RuO_2 at 10% intervals. No un-indexed reflections were observed and with the exception of the pure TiO_2 sample the diffraction peaks could be assigned to a rutile structure with *d*-spacings intermediate between those of pure TiO_2 and RuO_2. Additional peaks corresponded to reflections expected from the titanium metal substrate. It should be emphasised that the rutile peaks were relatively broad and weak, and provided no evidence for separate TiO_2- and RuO_2-rich phases. Using a slower scan rate (0·05° step min^{-1}) a more detailed analysis of the major peaks (1 1 0, 1 0 1, 2 1 1) confirmed the presence of a single broad peak in all cases. An example of the X-ray diffraction results for the composition (TiO_2:RuO_2, 70:30) is shown in Fig. 1, and data for other compositions are also available [15].

Using the information from the slow scan rate experiments it was possible to plot the rutile *d*-spacing (1 1 0 and 2 1 1 reflections) as a function of composition for the series of coatings. These results are shown in Fig. 2a and b and exhibit a marked deviation from Vegard's law. The crystallite size within the coatings was calculated from the extent of line broadening and found to be 25–35 nm for all RuO_2–TiO_2 ratios in good agreement with the observations of Pizzini *et al.* [9].

Table 1. Lattice constants of RuO_2 *and* TiO_2

Material	a_0	c_0	*Reference*
RuO_2 crystal	4·491	3·106	this work
RuO_2 crystal	4·4906	3·1064	19
RuO_2 crystal	4·4980	3·1084	17
RuO_2 coating	4·506	3·111	this work
		3·13	9
TiO_2 crystal (rutile)	4·594	2·958	19
TiO_2 anatase	3·783	9·51	16

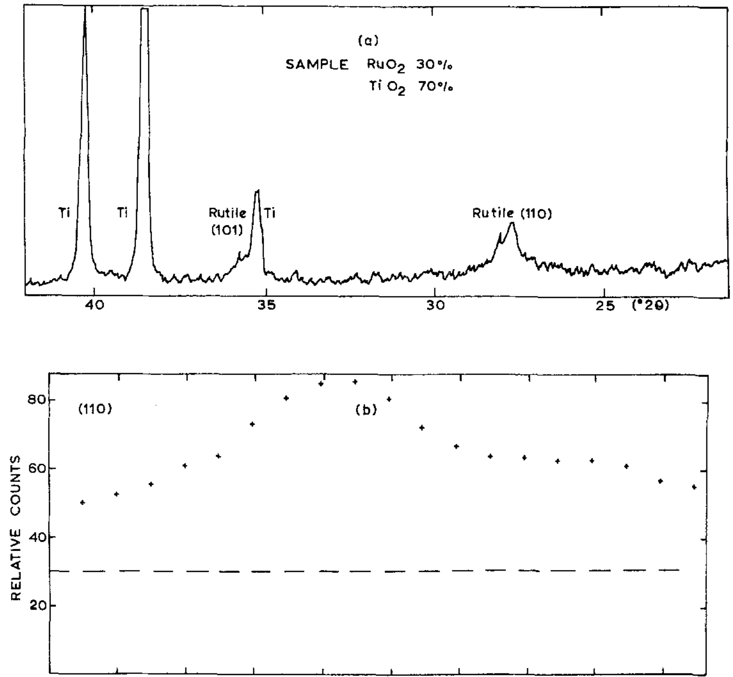

Fig. 1. X-ray diffraction scan of mixed oxide coating (TiO_2:RuO_2, 70:30) on titanium substrate; (a) fast scan 1° min^{-1}, (b) slow scan, 0·05° step min^{-1} of (1 1 0) peak.

The structure of the mixed oxide coatings was further investigated by examination of the samples prepared on silica optical flats using the established procedure and firing at 400° C. The X-ray diffraction curve for the composition (TiO_2:RuO_2, 70:30) is reproduced in Fig. 3a and the rutile peaks have similar characteristics to those exhibited by the oxide coatings prepared on titanium substrates (compare with Fig. 1). The only difference is the presence of a few lines which could not be indexed; these disappeared on annealing at 400° C for $3\frac{1}{2}$ hours (Fig. 3b).

Selected coatings prepared on silica were refired at 800° C in air for different periods. Under these conditions examination of the X-ray diffraction chart revealed that the rutile peaks corresponding to the 1 1 0 reflections ($2\theta = 27$–$28°$) and 1 0 1 reflections ($2\theta = 35$–$36°$) were split indicating the presence of separate RuO_2- and TiO_2-rich phases. This process occurred quickly and completely for samples with low RuO_2 content and systematically more slowly as the RuO_2 concentration increased. The results for the composition TiO_2:RuO_2, 70:30 (compare with Figs. 1 and 3) are reproduced in Fig. 4 and for the composition TiO_2:RuO_2, 90:10 in Fig. 5. The latter diagram also includes the results of a slow step scan which depicts the line splitting more clearly for this composition. The peaks corresponding to the RuO_2- and TiO_2-rich phases gave *d*-spacing values within 1% of those expected for pure TiO_2 and RuO_2 indicative of only very limited solid solubility.

The general features of the preceding X-ray diffraction observations are in accordance with the results recently reported by Hine *et al.* [11] who also reported broad X-ray peaks for coatings prepared at 450° and the development of peak splitting when the coatings were subsequently heated to 700° C.

It would appear, therefore, that the preparation technique which involved firing the reagents in air either at 400° C (present work) or at 450° C [11] produced a meta-stable 'TiO_2–RuO_2' solid solution or an extremely finely dispersed mixture of the two phases. Upon firing at higher temperatures (700–800° C) the constituent ions appear to have sufficient mobility to establish the equilibrium situation in which almost pure rutile TiO_2 and RuO_2 phases co-exist with only limited solid solubility. To check that the TiO_2–RuO_2 system exhibits a wide miscibility gap, a variety of reagents and procedures [15], including hot pressing at 1100° C, were employed in an endeavour to

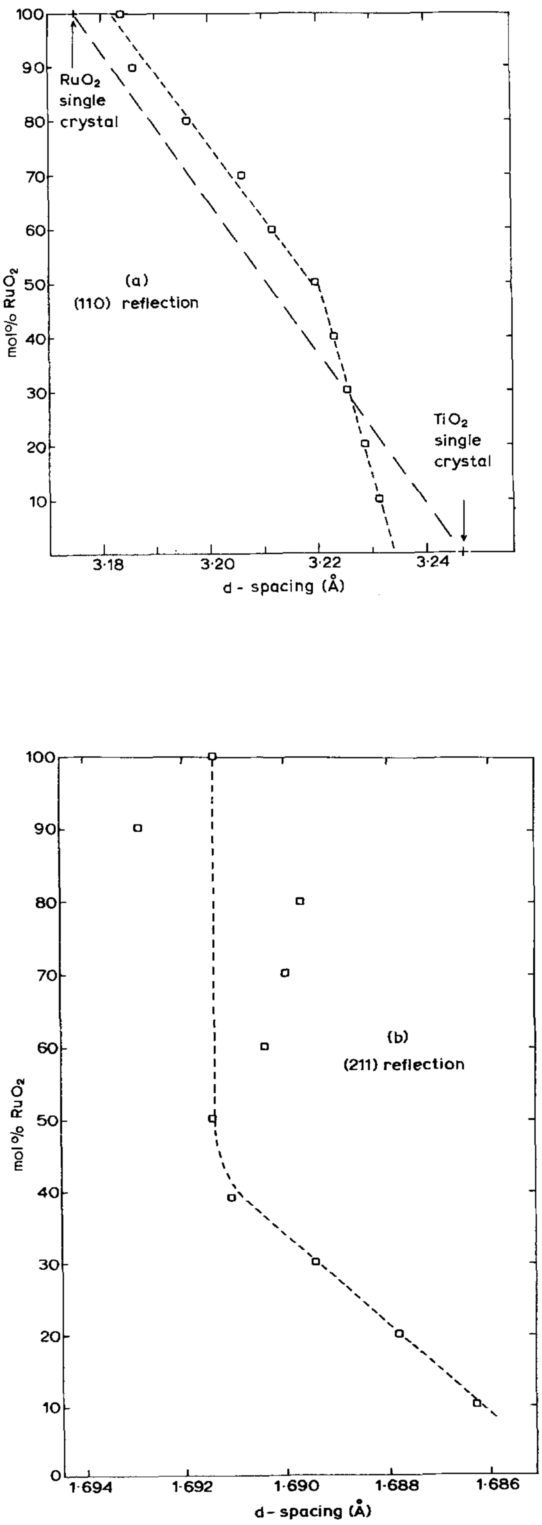

Fig. 2. d-spacing of rutile type structure on mixed oxide coating as a function of RuO_2 content; (a) (1 1 0) reflection, (b) (2 1 1) reflection.

prepare a solid solution, but all attempts were unsuccessful and no significant solid solution ($< 1{\cdot}5\%$) was detected. These observations have been confirmed by Dunn [20] and also by Zeeman [21] who demonstrated that negligible solid solution occurred even after heating together 10 nm RuO_2 and TiO_2 powders for more than 200 hours at 1000° C.

The absence of significant solid solution between rutile RuO_2 and TiO_2 may appear surprising as the constituent oxides appear to satisfy the requirements of the Hume–Rothery rules for solid-solution formation. However the electronic and lattice properties of the two oxides differ considerably. For example, deviations from stoichiometry are accommodated in TiO_2 by the formation of crystallographic shear planes [12] whereas there is no evidence for similar defects in non-stoichiometric RuO_2 [22], an observation which might be attributed to different dielectric constants for the two phases [23]. In this context it is perhaps significant that non-stoichiometric TiO_2 and VO_2 both exhibit crystallographic shear defects and also form extensive solid solutions at ambient temperatures [24].

As already mentioned, the general features of the effect of temperature upon the X-ray diffraction peaks are similar to those reported by Hine [11]. It should be noted, however, that the relatively long annealing time at 400° C used in the present work always produced mixed oxide coatings containing an insignificant amount of anatase even when applied to silica substrates (Fig. 3). It does not appear, therefore, that titanium metal must be present to encourage the anatase–rutile transformation as observed by Hine *et al.* [11], and indeed a mixed oxide coating on a platinum substrate prepared by these workers at 450° C also exhibited only the rutile structure.

Significant quantities of anatase were observed in the present investigation only when the isopropanol solution contained $TiCl_4$ alone. The introduction of small quantities of $RuCl_3$ (5–10 mol%) to the isopropanol solution was sufficient to stabilize the rutile TiO_2 form relative to anatase after the annealing treatment. This information is summarized in Fig. 6 which compares the relative quantities of anatase as a function of composition detected in the present investigation with those reported by Veselovskaya *et al.* [5].

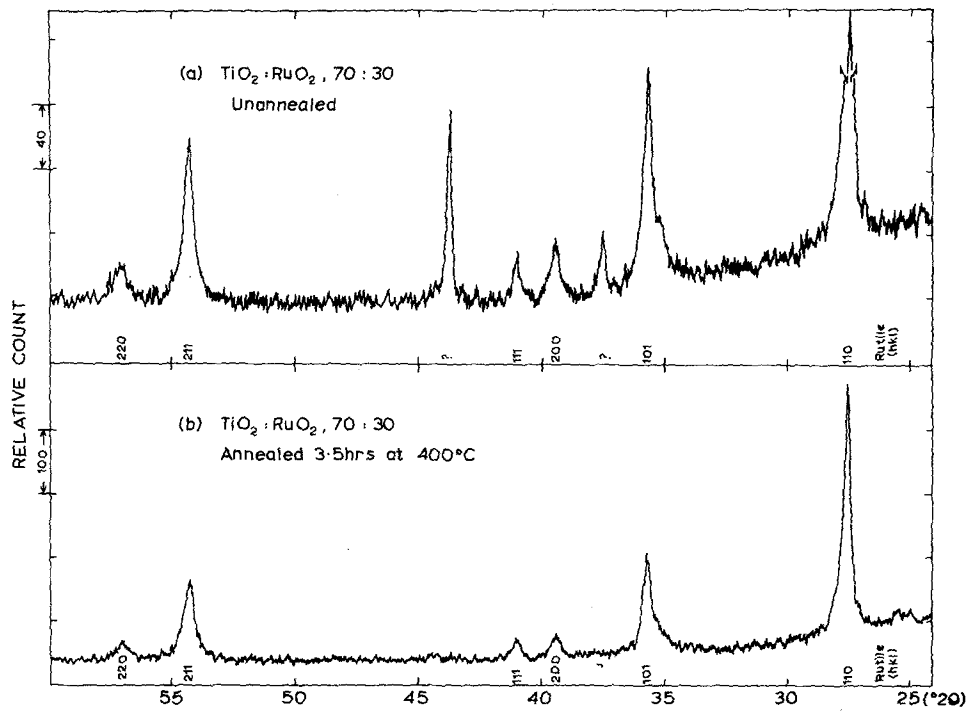

Fig. 3. X-ray diffraction scans of mixed oxide coating (TiO$_2$:RuO$_2$, 70:30) on silica substrates; (a) not annealed, (b) annealed $3\frac{1}{2}$ h at 400° C.

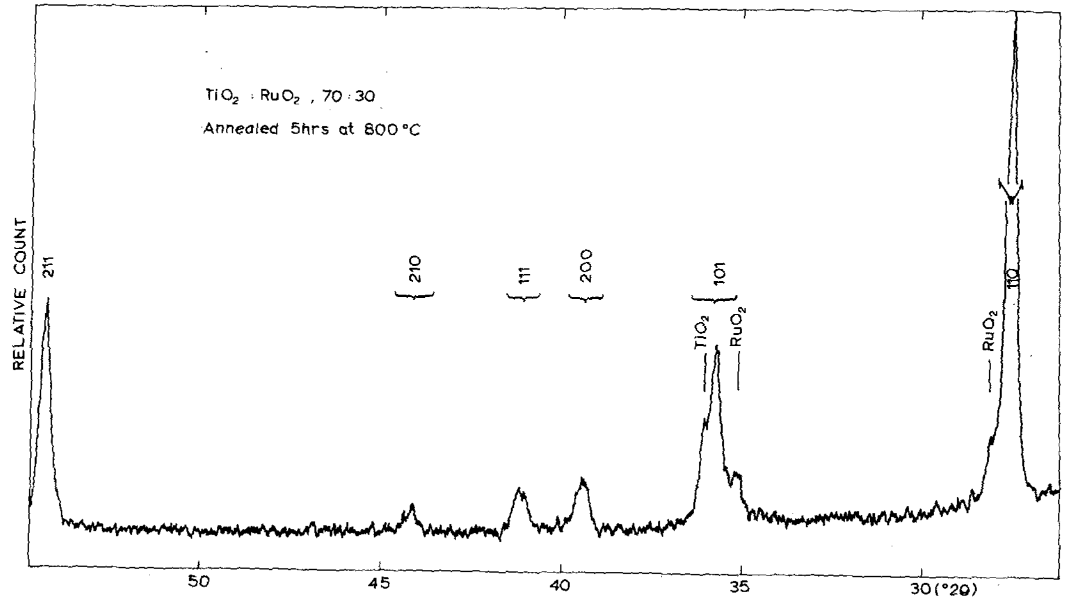

Fig. 4. X-ray diffraction scan of mixed oxide coating (TiO$_2$:RuO$_2$, 70:30) on silica substrate after annealing at 800° C for 5 h.

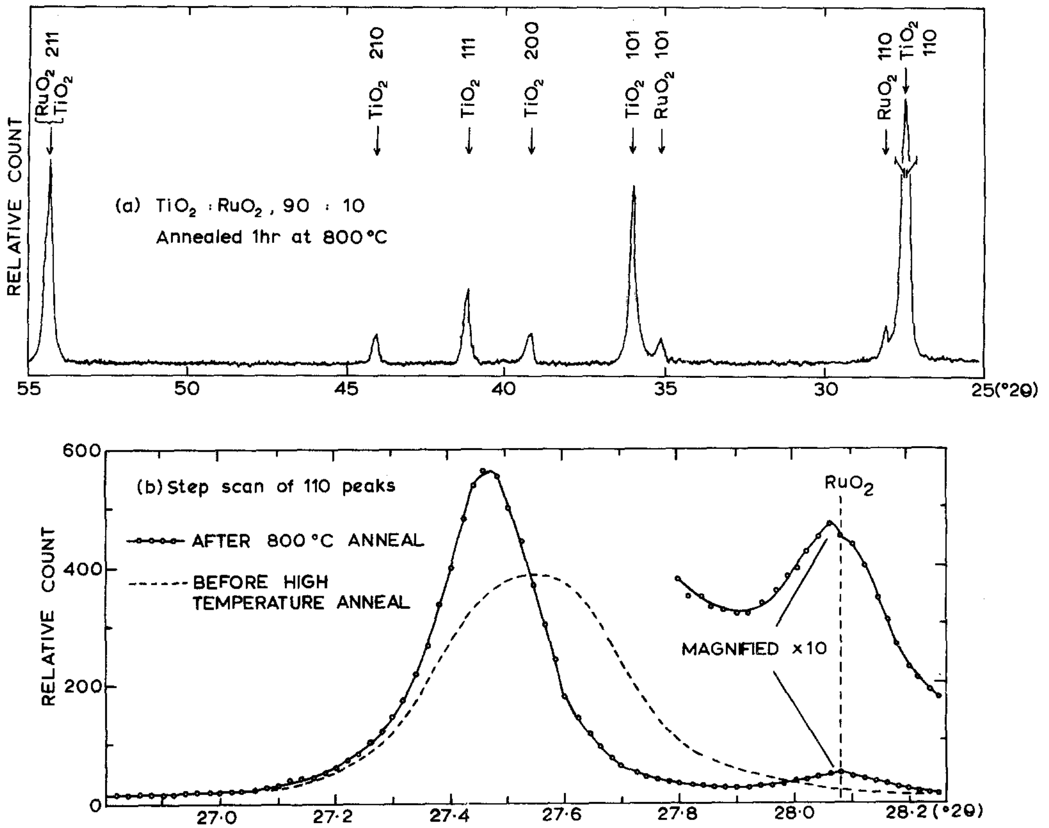

Fig. 5. X-ray diffraction scan of mixed oxide coating (TiO_2:RuO_2, 90:10) on silica substrate after annealing at 800° C for 1 h; (a) fast scan 1° min^{-1}, (b) slow scan, 0·05° step min^{-1}, of (1 1 0) peak.

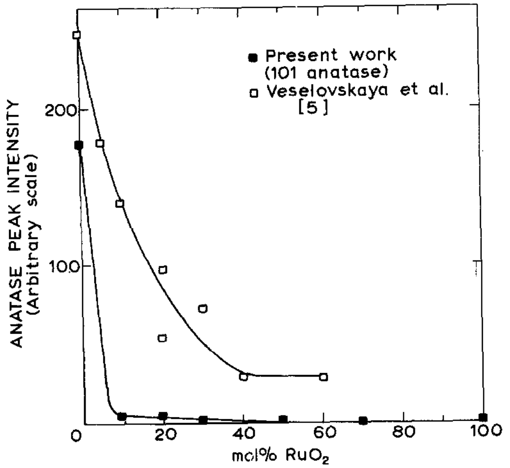

Fig. 6. Anatase content of mixed oxide coating as a function of composition.

Additional studies were also undertaken to provide more information about the microstructural characteristics of the mixed oxide coatings. Scanning electron micrographs revealed [15] the cracked dried-mud surface structure already reported [9] for all samples regardless of RuO_2 content. It was impossible to monitor the chlorine content of the coatings by EPMA because of interference between the chlorine and ruthenium emissions. It is known, however, from chemical analysis [9] and the measurement of concentration profiles in oxide coatings using secondary ion mass spectrometry [25, 26], that significant quantities of chlorine (up to 4 wt%) are present in all coatings prepared at temperatures lower than 800° C. The presence of chlorine can be expected to influence the electrical conductivity, relative stabilities of anatase and rutile, and development of the operational microstructure. More information is urgently required about the role of this element in mixed oxide coatings.

4. Conductivity measurements and discussion

The resistivity values of the oxide coatings prepared on the sections of silica tube were measured as described. As the resistivity was expected to be a complex function of composition, coating thickness, temperature and duration of firing oxygen partial pressure, it was decided initially to maintain the firing temperature at 400° C for all coatings and to investigate the effect of firing time. Normally 5 or 6 applications were required to produce an oxide coating approximately 2μm thick and the manner in which the resistance changed with increasing thickness is shown in Fig. 7 for the composition TiO_2:RuO_2, 70:30.

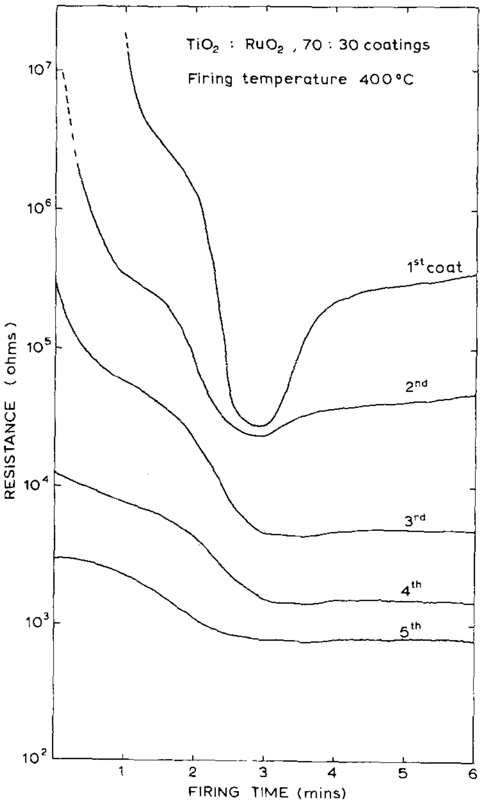

Fig. 7. Resistivity of TiO_2:RuO_2, 70:30 coating on silica substrate as a function of number of coatings and firing time at 400° C.

If it is assumed that the resistivity values monitor the development of the various chemical phases and associated microstructure then the curves depicted in Fig. 7 also imply that the major structural changes are completed in approximately 3–5 min at 400° C. To investigate any influence of kinetically slower processes, selected compositions were annealed for longer periods at 400° C. Fig. 8 indicates that the resistivity of pure RuO_2 coatings stabilized after 5 min annealing but the 70:30 (TiO_2:RuO_2) coating required about 1½ hours treatment before attaining a steady resistivity value. X-ray examination of coatings subjected to long anneals tended to support the resistivity measurements in that the diffraction scan for pure RuO_2 coatings indicated only a slight increase in line intensity whereas significant structural re-arrangements were occurring within the coatings containing significant quantities of TiO_2. Examination of the 70:30 (TiO_2:RuO_2) coating, for example, revealed that certain unindexed reflections disappeared after 3½ hours annealing at 400° C (see Fig. 3).

Annealing the mixed oxide coatings will undoubtedly produce a more consistent material

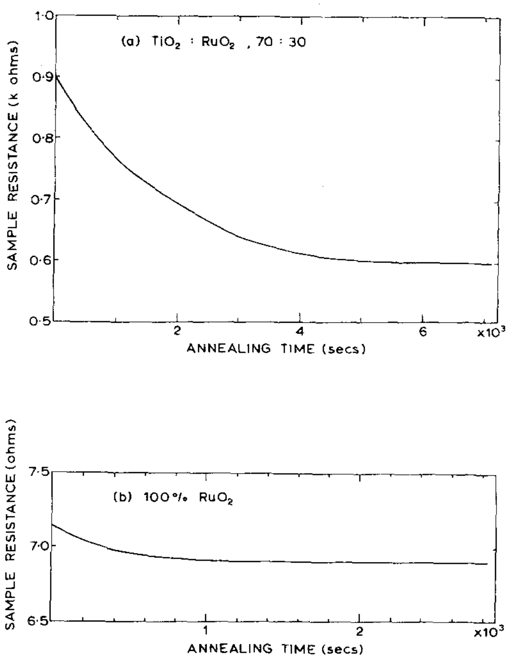

Fig. 8. Resistivity of mixed oxide coatings on silica substrate as a function of annealing time at 400° C; (a) TiO_2:RuO_2, 70:30 composition; (b) RuO_2, 100%.

but if the substrate is titanium then thermal oxidation of the metal may occur which can considerably increase the overall resistance of the system; usually the temperature and duration of firing are optimized to produce the required electrochemical properties. It is interesting to note, therefore, that the investigations of Hine *et al.* [11] indicate that 5 min firing at 450° C produced a coating on titanium with the minimum d.c. resistance and also with the minimum polarization resistance as determined by electrochemical measurements. Coatings prepared at higher temperatures on platinum substrates had lower resistances which is in accordance with the findings of the present work that longer annealing times at 400° C produced lower resistivity values. However, the electrochemical activity of the platinum coatings prepared at high temperatures was inferior to that of titanium-based coatings prepared at 400° C. Whether this effect is due to loss of activity or decrease in surface area is not stated, but the electrochemical behaviour of titanium based coatings annealed for relatively long periods (10 hours) at 400° C is described in a subsequent paper [27].

The temperature dependence of the resistivity was also measured for selected coatings on the silica tube substrates and considerable hysteresis was observed. There was no doubt, however, that the temperature coefficient of the resistivity was negative which is a typical property of semiconducting materials and is in agreement with other investigations [3, 11].

The variation in conductivity of the oxide coatings on silica as a function of composition is shown in Fig. 9. The general features of this curve are in accordance with the expected behaviour of a mixture of conducting and insulating oxide particles according to percolation theory [28, 29] which predicts a relationship of the type

$$\sigma \propto (x - x_c)^p$$

where x_c is a critical composition (0·25–0·33) and p is a constant (1·4–1·7). The linear relationship between log σ and the reciprocal of the RuO_2 content depicted in Fig. 10 is also in accordance with percolation theory. The significance of the relationship between resistivity and composition will be discussed in a second paper [27] concerned with the electrochemical properties of oxide-coated anodes.

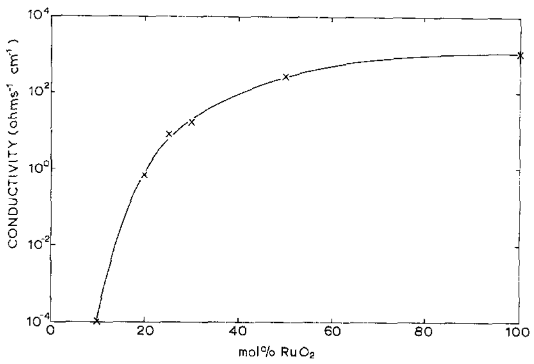

Fig. 9. Conductivity of mixed oxide coatings annealed for six hours on silica substrates as a function of composition.

5. Conclusions

X-ray diffraction data suggest that the oxide coatings prepared at 400° C on titanium and silica substrates consist of a meta-stable solid solution of RuO_2 and TiO_2 having a crystallite size of around 25 nm. The fine detail of the microstructure is influenced by the temperature and duration of firing and requires further examination in a scanning transmission electron microscope.

The structural changes within the oxide coatings can be monitored by resistivity measurements, whilst the dependence of resistivity upon coating composition exhibits a relationship more indicative of a finely interdispersed mixture of conducting and insulating particles than an ideal solid solution.

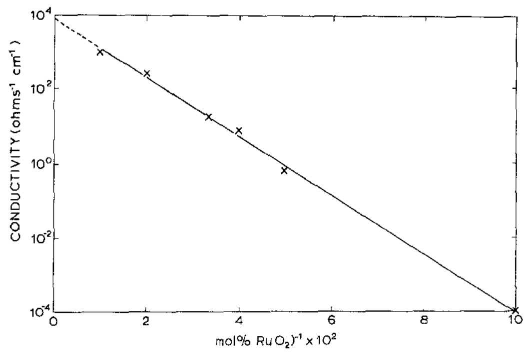

Fig. 10. Log conductivity of mixed oxide coatings versus reciprocal of RuO_2 content.

Acknowledgements

Financial support for one of us (WAG) from Albright and Wilson is gratefully acknowledged.

References

[1] K. Hase and P. Schmittinger, *Electrochim. Acta* **21** (1976) 1115.

[2] G. Faita and G. Fiori, *J. Appl. Electrochem.* **2** (1972) 31.

[3] A. T. Kuhn and C. J. Mortimer, *J. Electrochem. Soc.* **120** (1973) 231.

[4] D. Galizzioli, F. Tantardini and S. Trasatti, *J Appl. Electrochem.* **4** (1974) 57.

[5] I. E. Veselovskaya, E. K. Spasskaya, V. A. Sololov, V. I. Tkachenko and L. M. Yakimenko, *Elektrokhimiya* **10** (1974) 70.

[6] D. Galizzioli, F. Tantardini and S. Trasatti, *J. Appl. Electrochem.* **5** (1975) 203.

[7] I. R. Burrows, J. H. Entwisle and J. A. Harrison, *J. Electroanalyt. Chem.* 77 (1977) 21.

[8] T. Arikado, C. Iwakura and H. Tamura, *Electrochim. Acta* **22** (1977) 513.

[9] S. Pizzini, G. Buzzanca, C. Mari, L. Rossi and S. Torchio *Mat. Res. Bull.* 7 (1972) 449.

[10] K. J. O'Leary and T. J. Navin, Abstract 257, Electrochemical Soc. Extended Abstracts, Spring Meeting, San Francisco, California (May, 1974) p. 603.

[11] F. Hine, M. Yasuda and T. Yoshida, *J. Electrochem. Soc.* **124** (1977) 500.

[12] L. A. Bursill and B. G. Hyde, 'Progress in Solid State Chemistry', (eds. H. Reiss and J. O. McCaldin) Vol. 7, Pergamon Oxford (1972) p. 177.

[13] J. B. Goodenough, 'Progress in Solid State Chemistry', (ed. H. Reiss), Vol. 5, Pergamon, Oxford (1971) p. 145.

[14] R. M. Peekema and M. W. Shafer, *J. Electrochem. Soc.* **123** (1976) 1779.

[15] W. A. Gerrard, PhD Thesis, University of London (1976).

[16] L. G. Berry (ed.), A.S.T.M. Index, Amer. Soc. for Testing Mats. Pa, USA.

[17] G. Bayer and H. G. Wiedemann, *Thermochem. Acta* **11** (1975) 79.

[18] C. E. Boman, *Acta Chem. Scand.* **24** (1970) 116.

[19] D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, *Inorg. Chem.* 8 (1969) 841.

[20] P. Dunn, DPhil. Thesis, University of Oxford (1977).

[21] G. Zeman, MSc Thesis, University of Purdue, USA (1974).

[22] M. Storey, private communication.

[23] L. A. Bursill, B. G. Hyde and M. O'Keefe in 'Solid State Chemistry', (eds. R. S. Roth and J. S. Schneider) N.B.S. Special Publ. 364, National Bureau of Standards, Washington (1972) p. 197.

[24] I. K. Kristenson, *J. Appl. Phys.* 39 (1968) 5341.

[25] T. Arikado, C. Iwakura and H. Tamura, *Electrochim. Acta* 22 (1977) 229.

[26] T. Arikado, C. Iwakura and H. Tamura, *Electrochim. Acta* 22 (1977) 513.

[27] W. A. Gerrard, B. C. H. Steele and J. H. E. Jeffes, *J. Appl. Electrochem.*, to be published.

[28] R. B. Stinchcombe, *J. Phys. Soc. C* 7 (1974) 179.

[29] B. Abeles, H. L. Pinch and J. L. Gittleman, *Phys. Rev. Lett.* **35** (1975) 247.