

## Effect of Chlorine on Solid Solution Formation in Ruthenium Titanium Dioxide Coatings

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Rutile-type dioxides of titanium and ruthenium form partial solid solutions at temperatures above 1000°C, whereas the miscibility is complete in the temperature range of 350–600°C, when the oxides are coated on titanium or alumina substrates. The present work tends to show that the  $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$  coatings are metastable solutions wherein the chloride ions are likely to replace the oxide ions on the sublattice  $\text{O}^{2-}$  sites. The increase of  $a$  and  $c$  parameters in the overall composition range are compatible with a Cl/Ru ratio of 2.5 at.% in the rutile lattice. This ratio does not depend upon the titanium content and therefore it is thought that the  $\text{Cl}^-$  ions are compensated by reduced  $\text{Ru}^{3+}$  (or  $\text{Ti}^{3+}$ ) species. The electrical conductivity retains its metal-like characteristics in the composition range of 30–100%  $\text{RuO}_2$ , this is accounted for by the existence of Ru-O  $\pi^*$  bands along (110) directions. The reduced ions in equilibrium with  $\text{Cl}^-$  would provide additional paths for electron transport along the  $c$ -axis, explaining the high values of conductivity in the concentration range of 30–50%  $\text{RuO}_2$ .

### Introduction

Ruthenium dioxide  $\text{RuO}_2$  is a rutile-type oxide which is known to form solid solutions with  $\text{TiO}_2$  when oxide powders are heated above 1000°C. The investigations of several Russian authors (1, 2) show that the limits of solubility in the  $\text{RuO}_2$ - $\text{TiO}_2$  system are 8%  $\text{TiO}_2$  in  $\text{RuO}_2$ , and 10%  $\text{RuO}_2$  in  $\text{TiO}_2$  at 1100°C. On the other hand, the  $\text{RuO}_2$ - $\text{TiO}_2$  coatings synthesized between 350 and 600°C as anodes for chlorine evolution, consist of more or less complete solid solutions (3–5). According to Gerrard and Steele (3) the coatings are best described as a metastable solid solution since separated X-ray diffraction peaks corresponding to almost pure  $\text{RuO}_2$  and  $\text{TiO}_2$  phases are encountered at higher temperature (700–

800°C). However, the resistivity–composition relationship might indicate that an extremely fine mixture of the two components is formed at low temperatures (3).

As the mixed oxide coatings are usually prepared from  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$ , a residual amount of chlorine is observed beyond 800°C (4, 6–8). For this reason, Roginskaya (4) considers that the mixed  $\text{RuO}_2$ - $\text{TiO}_2$  coatings consist of a pseudo-binary system  $\text{RuO}_2$ - $\text{TiO}_2$ -Cl.

This hypothesis would explain why the miscibility is complete at low temperatures whereas it is only partial at temperatures higher than 1000°C.

The role and the location of Cl in the  $\text{RuO}_2$  layers have been discussed in two review papers by Trasatti and Lodi (9) and Trasatti and O'Grady (10). The oxygen defi-

ciency observed below 800°C, making it likely that Cl is in the oxygen lattice position. This hypothesis is also supported by the larger lattice parameters of low-temperature RuO<sub>2</sub> layers relative to the single crystal (11). In the case of TiO<sub>2</sub>-RuO<sub>2</sub> coatings, less information is available from crystallographic studies, and there is no experimental evidence for the presence of chlorine in the rutile lattice.

In order to provide additional information about the effect of chlorine on the formation and stability of RuO<sub>2</sub>-TiO<sub>2</sub> solid solutions, samples were prepared at different temperatures from chlorides and organic compounds of Ti and Ru. Examinations of the microstructure, accurate measurements of lattice parameters, and electrical conductivity studies have been performed as a function of temperature, annealing time, and composition.

## Experimental

Investigations were carried out on RuO<sub>2</sub>-TiO<sub>2</sub> coatings prepared on either flat titanium sheets or alumina substrates for hybrid circuits (MRC superstrates). The titanium sheets had previously been etched in aqueous solutions of oxalic acid at 90°C. The coatings were prepared by mixing 0.4 M solutions of RuCl<sub>3</sub>·*x*H<sub>2</sub>O (or Ru(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>0.01</sub> M) and Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (or TiCl<sub>4</sub>) in isopropanol. The solutions were applied to the substrate by painting and allowed to dry prior to the firing. An alternative method consists of spraying the solution on the substrate heated at temperatures below 100°C. In both cases, several applications including the firing process (15 min at 350, 450, or 600°C) are necessary to form a coating thickness of 2–5 μm.

The microstructure and microanalysis of Ti and Ru were investigated by SEM (JEOL JSM 35 C equipped with an EDAX microanalyzer). The chlorine content was

measured by X-ray spectrometry. The apparatus is a Philips PW 1410 fitted with a Cr-target X-ray tube, a PET analyzing crystal, and a flow counter. ClK<sub>α</sub> and RuL<sub>β</sub> lines were recorded and compared.

The lattice parameters were calculated from the angular position of the (110) and (101) lines. The X-ray apparatus is a CGR σ2080 diffractometer. The monochromatized CuK<sub>α</sub> radiation of λ = 1.5405 Å was used. A step scanning device coupled with an automatic printer was used for recording the diffraction profiles with angular steps of 0.02 (2θ). The (012), (104), and (110) lines of Al<sub>2</sub>O<sub>3</sub> and the (010) and (002) lines of Ti from the substrates were used as standards. However, the most accurate results were obtained from alumina substrates because their structure is much less influenced by the firing conditions than the titanium substrates. The parameter accuracy is 0.1% for *a*, and 0.03% for *c*. The electrical measurements were carried out in a vertical furnace between room temperature and 600°C.

Electrical resistance was measured between two parallel platinum wires pressed on the sample and spaced 10 mm apart. A Keithley electrometer 212 D was used.

## Results

### 1. Chlorine Analysis

The Cl/Ru ratios (in at.%) of the mixed oxides are listed in Tables I and II. Values generally lower than 6 at.% are observed. For each temperature, the chlorine content is approximately constant with respect to Ru, whatever the Cl content might be in the titanium precursor used (TiCl<sub>4</sub> or Ti(OC<sub>3</sub>H<sub>7</sub>)), and does not depend on Ti content.

### 2. Solid Solution Formation

SEM examinations show the typical “cracked mud” texture of the coatings

TABLE I  
CHLORIDE CONTENT OF  $Ru_xTi_{1-x}O_2$  COATINGS PREPARED FROM  $RuCl_3 \cdot x H_2O$  AND  $Ti(OC_3H_7)_4$

Deposition process	Composition (at.% $RuO_2$ )	Substrate	Pyrolysis temperature ( $^{\circ}C$ )	Thickness ( $\mu m$ )	Cl/Ru (at.%)
Painting	27	Ti	350	2.06	4.1
	27	$Al_2O_3$		2.59	5.6
	48.5	$Al_2O_3$		2.56	4.8
	100	$Al_2O_3$		1.73	5
	27	Ti	475	1.35	5.15
	27	$Al_2O_3$		2.24	2.05
	48.5	Ti		0.87	4.1
	48.5	$Al_2O_3$		1.71	2.95
	77	$Al_2O_3$		11.69	4.15
	100	$Al_2O_3$		1.3	3.45
	27	Ti		600	4.6
	27	$Al_2O_3$	7.13		3.05
	48.5	Ti	4.34		2.75
	48.5	$Al_2O_3$	4.5		4.1
	77	Ti	8.1		3.2
Spray	48.2	$Al_2O_3$	600	1.64	2
	100	$Al_2O_3$		1.4	2.3

(Fig. 1a). The X-ray micrographs (Figs. 1b and c) show that the distribution of Ti and Ru is homogeneous in the micrometer range. The X-ray diffraction spectra of the  $TiO_2$ - $RuO_2$  coatings correspond to the rutile structure. Traces of anatase are, however, detected in samples containing less than 20%  $RuO_2$ . The mean peak positions lie between those of pure  $RuO_2$  and pure  $TiO_2$  rutile-type phases. The peak profiles are broadened in much the same way for pure  $RuO_2$  and any Ti-containing composition. In addition, their symmetrical shape suggests that peak broadening is mainly due to crystallite-size effect rather than to a mixing of solid solutions of different compositions.

A mean crystallite size has been determined from X-ray broadening measurements using the Anatharaman and Christian relation (14) applied to the integral breadth of experimental and instrumental profiles. The values range between 6 and 9 nm for

samples prepared at 475 $^{\circ}C$  and between 10 and 18 nm at 600 $^{\circ}C$ .

The lattice parameters  $a$  and  $c$  of the  $RuO_2$ - $TiO_2$  coatings are plotted as a function of the composition (Figs. 2a and b). The values of parameter  $a$  are in agreement with Vegard's law except for the highest  $RuO_2$  contents. For 100%  $RuO_2$  a mean

TABLE II  
CHLORIDE CONTENT OF  $Ru_xTi_{1-x}O_2$  COATINGS PREPARED AT 475 $^{\circ}C$  FROM  $TiCl_4(1)$  AND  $Ti(OC_3H_7)_4(2)$  ON  $Al_2O_3$  SUBSTRATE

Composition (at.% $RuO_2$ )	Thickness ( $\mu m$ )	Lattice parameter $a$ ( $\text{\AA}$ )	Cl/Ru (at.%)
(1) 55	2.2	4.544	4.2
(1) 63	2.8	4.533	6.4
(1) 85	2.2	4.508	5.4
(2) 48	2.5	4.545	5.1
(2) 63	2.9	4.534	5.1
(2) 82	1.9	4.511	5.1

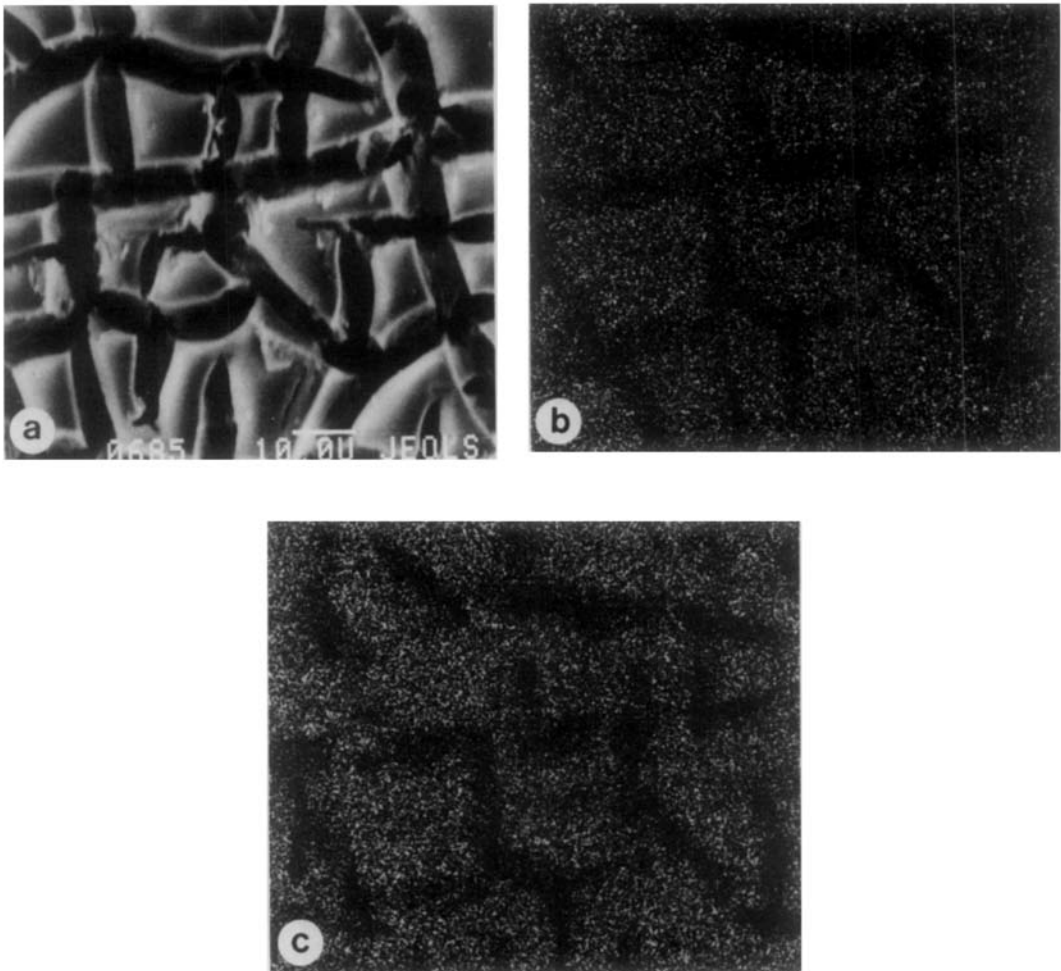


FIG. 1. Microstructure of a Ru<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub> coating where  $x = 0.77$ , by SEM. (a) Electron image. (b) X-Ray image of Ru. (c) X-Ray image of Ti.

value of 4.520 Å is observed, instead of the usually observed value 4.490 Å (13, 14). On the other hand, the  $c$  parameter increases linearly with the Ru content (Fig. 3b) but the slope of the function is greater than that of Vegard's law, so that a value of 3.141 Å is obtained for pure RuO<sub>2</sub> instead of the normal value of 3.106 Å.

The above results are independent of the nature of the substrate. The only difference is the better adhesion of the coatings on titanium. This can be explained by the for-

mation of a thin rutile-TiO<sub>2</sub> layer at the Ti-RuO<sub>2</sub> interface, which is observed by X-ray diffraction when a titanium sheet is coated with pure RuO<sub>2</sub>.

Attempts have been made to synthesize RuO<sub>2</sub>-TiO<sub>2</sub> solid solutions in absence of chlorine.

A 50:50 mixture (in at.%) of Ru(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> and Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> in isopropanol was prepared by painting Al<sub>2</sub>O<sub>3</sub> substrates and heating them at 475°C. Owing to the weak solubility of Ru(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub> in isopro-

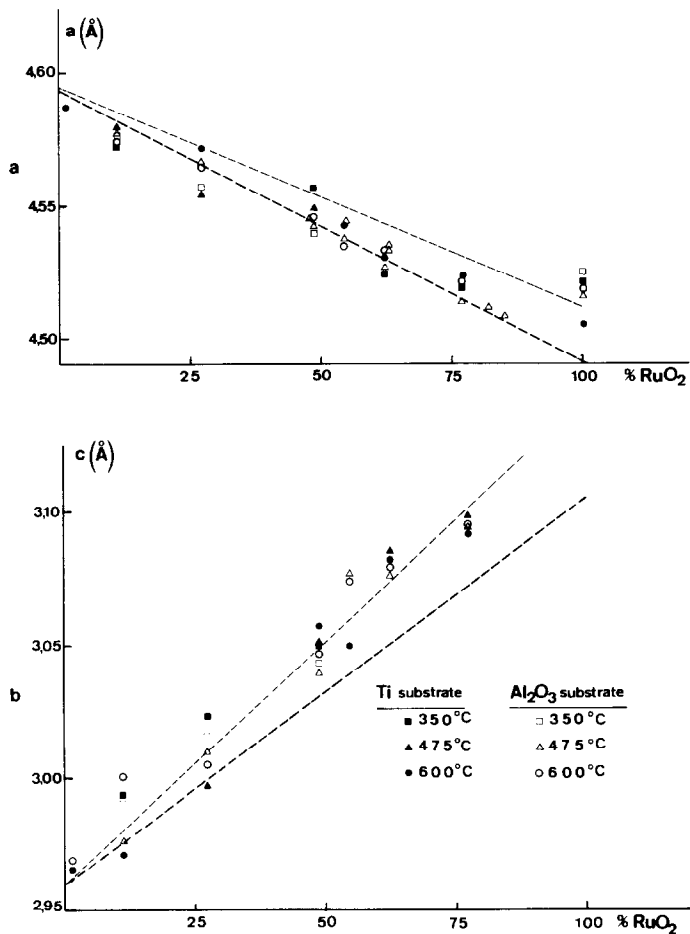


FIG. 2. Lattice parameters of  $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$  solid solutions as functions of the composition. (a) Parameter *a*. (b) Parameter *c*. —, Vegard's function. ---, Calculated from present model assuming that the Cl/Ru ratio is 2.5 at. %.

panol, the procedure of painting and firing was repeated more than 10 times until a layer thickness of  $\approx 0.7 \mu\text{m}$  was attained. The  $\text{RuO}_2$  content after treatment was 30 at. %. Instead of the "dried mud" structure, a fine grained matrix was observed. The (110) peak profile was strongly broadened. Its maximum at  $27^\circ 60'$  corresponded with a solid solution of the above composition. However, the asymmetrical shape of the peak, its strong broadening, and the local variations of composition detected by SEM, suggest that several solid composi-

tions might have been formed. On the other hand, its resistivity (1.4 cm) is substantially lower than that of Cl-containing samples (Fig. 5).

Further attempts were made in order to check the stability of the  $\text{RuO}_2\text{-TiO}_2$  solid solutions, as a function of the chlorine content measured during annealing treatments. A series of samples coated on alumina at  $475^\circ\text{C}$  and containing 30%  $\text{RuO}_2$  was subjected to an isothermal treatment at  $600^\circ\text{C}$ . During this treatment, the chlorine content slowly decreased (Table III). The diffrac-

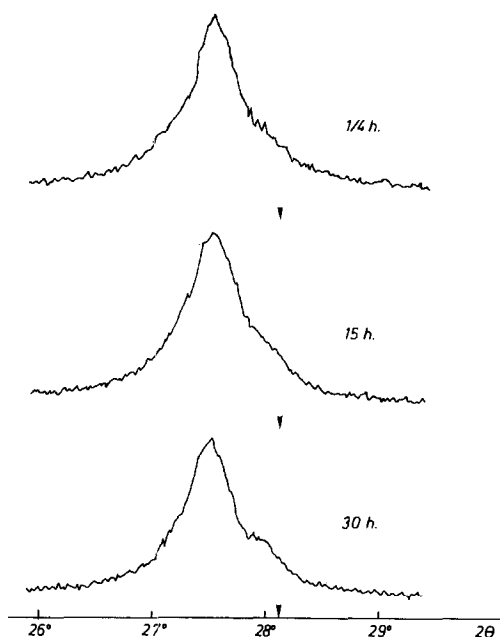


FIG. 3. X-Ray diffraction of {110} peaks of coatings containing 30% RuO<sub>2</sub> heated at 475°C. Decomposition is shown by the appearance of the {110} peak of RuO<sub>2</sub> near  $2\theta = 28.125^\circ$ .

tion profiles recorded at different times (Fig. 4), indicate a progressive decomposition of the solid solution because of (i) the angular shift toward the pure rutile TiO<sub>2</sub>

TABLE III  
CHLORIDE CONTENT  
AS A FUNCTION OF  
ANNEALING TIME AT  
475°C IN Ru<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>2</sub>  
COATED ON ALUMINA  
(4 LAYERS; MEAN  
THICKNESS = 4.4 μm,  
PYROLYSIS TIME FOR  
EACH LAYER = 15  
min)

Time (hr)	Cl/Ru (at. %)
0.25	2.52
1	2.47
15	2.40
54	2.25

profile and (ii) the appearance of an additional peak corresponding to the presence of pure RuO<sub>2</sub>.

### 3. Conductivity Measurements

The electrical conductivity at room temperature of mixed oxide coatings has been plotted as a function of the concentration in Fig. 5. Figure 6 results from measurements of conductivity in the temperature range 25–600°C after heating the samples for 1 hr at 600°C in order to stabilize the chlorine content. This figure indicates that the temperature coefficient of conductivity is negative for compositions higher than 30% RuO<sub>2</sub>, whereas it becomes positive for lower compositions.

The metal–semiconductor transition is evidenced in Fig. 5 by the change of slope of the conductivity occurring between 20 and 30% RuO<sub>2</sub>.

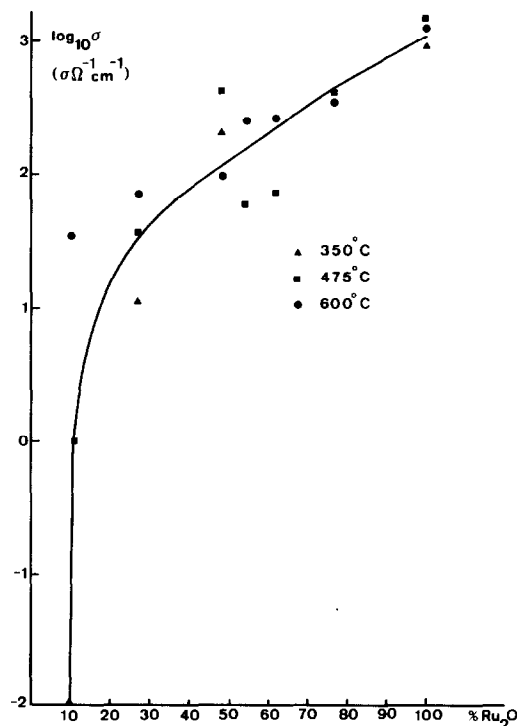


FIG. 4. Electrical conductivity of RuO<sub>2</sub>-TiO<sub>2</sub> coatings as a function of the composition.

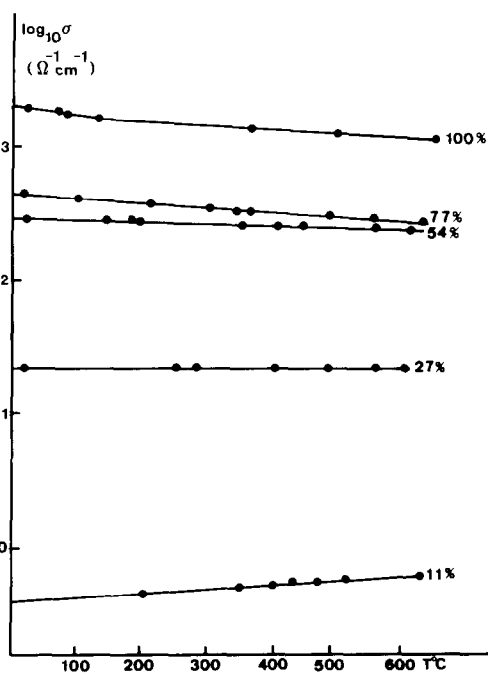


FIG. 5. Electrical conductivity of  $\text{RuO}_2\text{-TiO}_2$  coatings as a function of the temperature.

## Discussion

### 1. Lattice Parameters

The above results confirm that (i) detectable amounts of Cl are incorporated with the  $\text{RuO}_2\text{-TiO}_2$  coatings; (ii) the Cl content decreases with increasing time and temperature. However, attention must be paid to several important points:

(a) For similar experimental conditions (Table II), the Cl/Ru atomic ratio does not depend on the chlorine content of the  $\text{TiO}_2$  starting material;

(b) The Cl/Ru ratio apparently does not depend on the titanium content of the coatings;

(c) The Cl/Ru ratio is generally less than 0.06 and slowly decreases toward 0.02 after long annealing times at  $600^\circ\text{C}$ ;

(d) In absence of chlorine, the composition is not homogeneous at the micrometer scale.

Results in Tables I and II suggest that the chlorine content is related to some ion or defect associated with Ru, either in a  $\text{RuCl}_3$ -like compound or in the rutile lattice:

(1) Owing to the chlorine evolution between  $300$  and  $350^\circ\text{C}$  in the decomposition process of  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$ ,  $\text{RuCl}_3$  crystals may be formed in this temperature range (15, 16), and these coexist with  $\text{RuO}_2$  at higher temperature, when the furnace is insufficiently aerated. For instance, when the thermal decomposition of  $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$  was carried out by DTA in nitrogen ( $p_{\text{O}_2} = 10 \text{ Pa}$ ), the powder showed the  $\text{RuO}_2$  X-ray lines and some extra lines after heating ( $6^\circ\text{C}/\text{min}$ ) up to  $650^\circ\text{C}$ . The main peaks ( $d = 5.05, 3.40, 3.94, 2.45 \text{ \AA}$ ) were compatible with those reported by Fletcher *et al.* for  $\alpha\text{-RuCl}_3$  (16). For the reaction:  $\text{RuCl}_3 + \text{O}_2 \rightarrow \text{RuO}_2 + \frac{3}{2} \text{Cl}_2$ , the thermodynamic data (17) show that at  $700^\circ\text{K}$ , for example,  $\text{RuO}_2$  and  $\text{RuCl}_3$  may coexist if  $p_{\text{O}_2}/p_{\text{Cl}_2}$  is less than  $3 \times 10^{-3}$ .

(2)  $\text{Cl}^-$  may replace some oxygen in lattice sites. This would call for the presence of additional electrons or  $\text{Ru}^{3+}$  in cation sites to balance the difference in charge (10). The presence of  $\text{Cl}^-$  and  $\text{Ru}^{3+}$  in the

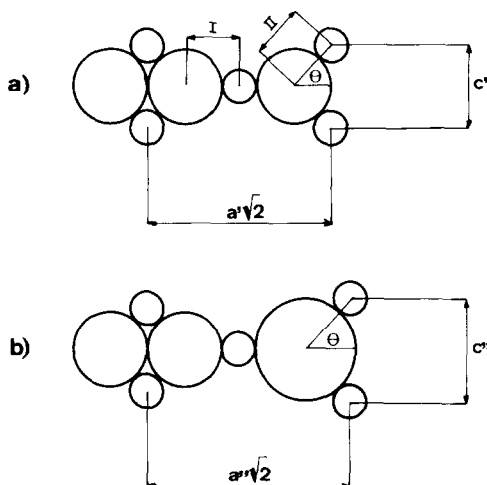


FIG. 6.  $\{110\}$  Planes of the rutile lattice. (a) Nonsubstituted. (b) Substitution of one  $\text{O}^{2-}$  by  $\text{Cl}^-$ .

lattice must result in a substantial increasing of  $a$  and  $c$  parameters. In case of pure RuO<sub>2</sub>, the present work and earlier research cited in the literature lead to larger parameters than in monocrystal (3, 7, 10). However, the introduction of Cl<sup>-</sup> and Ru<sup>3+</sup> in the rutile-like lattice is likely to be limited by the large ionic radii of these ions. This can be shown in a simplified model which assumes the replacement of oxygen by chlorine in the atomic ratio: 0.0125 (Cl/Ru = 0.025), corresponding with that found after annealing at 600°C (Table III).

Figure 6a shows a (110) plane of the rutile unit cell. Fig. 6b shows the same (110) plane where one of four oxygen ions of the unit cell has been replaced by one chloride ion.

The model consists of calculating the lengths of  $c''$  and of the diagonal  $a'' \sqrt{2}$  of the unit cell containing one Cl<sup>-</sup>. The  $a''$  and  $c''$  expansion is then averaged over 20 unit cells.

The  $a'$  and  $c'$  parameters result from Vegard's law. The bond lengths (M<sup>4+</sup>-O)<sub>I</sub> and (M<sup>4+</sup>-O)<sub>II</sub> are averaged from the known values of (Ru-O)<sub>I</sub> = 1.918 Å, (Ru-O)<sub>II</sub> = 1.998 Å, (Ti-O)<sub>I</sub> = 1.988 Å and (Ti-O)<sub>II</sub> = 1.944 Å. Ruthenium and titanium cations are assumed to form types I and II bonds with chlorine, wherein the chlorine ionic radius is assumed to change in the same manner as oxygen, while the ionic radii of Ru<sup>4+</sup> (0.62 Å) and Ti<sup>4+</sup> (0.61 Å) are kept constant in the  $a'$   $c'$  and  $a''$   $c''$  cells. This simplified model assumes in addition that the  $\theta$ -angle is kept constant when O<sup>2-</sup> is substituted by Cl<sup>-</sup>.

The calculated values of  $a''$  and  $c''$  are plotted as a function of the composition in Fig. 2. The effect of chlorine, assuming a Cl/Ru ratio of 0.025, results in a  $c$ -expansion of 1.0% and an  $a$ -expansion of 0.6% in pure RuO<sub>2</sub>, which is in accord with the parameter variations found in this study. Similar results were observed by Pizzini (7) who measured a lattice expansion of 0.7% along  $c$ -axis in low-temperature RuO<sub>2</sub>.

However, these parameters do not account for the Cl/Ru ratios found by some authors (7-9), which are 2 to 5 times greater than the above value. Consequently, it seems unlikely that amounts of Cl above 3% can enter into the RuO<sub>2</sub> rutile lattice unless other defects are considered. Oxygen vacancies are postulated to occur in pure RuO<sub>2</sub> (8). Also, the degree of non-stoichiometry as derived from the Ru and Cl content (10) is estimated to be up to 8.5% at 300°C. However, if one assumes that each oxygen vacancy is compensated by 2 Ru<sup>3+</sup> ions (ionic radius = 0.68 Å), one anticipates an increase in parameter, in accordance with experiments carried out at higher temperature (19, 20).

In the present experiments the increase of  $a$  and  $c$  parameters for high Ru contents (Fig. 2) is not systematically related to the temperature of preparation between 350 and 600°C. Furthermore, the variation of Cl content is weak (2-5 at.%) in this temperature range. From the above considerations it is believed that a fraction of chlorine, such that Cl/Ru is less than 0.03, can be maintained in the oxygen sites of the rutile lattice up to 800°C. The remainder should be involved in a dispersed RuCl<sub>3</sub>-like phase which is oxidized at lower temperature, depending on the furnace atmosphere.

The present model predicts that the departure from Vegard's law becomes less when TiO<sub>2</sub> is added to RuO<sub>2</sub>, because of the effect of chlorine dilution. The experimental values of parameter  $c$  found in the temperature range 350-600°C are consistent with a model assuming a Cl/Ru ratio of 0.025 in the lattice. The agreement is poorer in case of the  $a$  parameter which fits with Vegard's law in the range 10-80% RuO<sub>2</sub>. The present results apparently differ from these of Gerrard and Steele (3) who observed greater (110) spacings than those predicted by Vegard's law in the RuO<sub>2</sub>-rich side of the diagram and smaller values in the TiO<sub>2</sub>-rich side.

Nevertheless, both studies show that the



expansion of parameter  $a$  ascribed to Cl is limited to samples with high  $\text{RuO}_2$  content. In addition, recent results from Auger spectroscopy (21) indicate a detectable oxygen deficiency in the bulk of films prepared at  $475^\circ\text{C}$  and containing 30%  $\text{RuO}_2$ .

The defect structure of  $\text{TiO}_2$  certainly differs from that of  $\text{RuO}_2$  since, for example, deviations from stoichiometry are accommodated in  $\text{TiO}_2$  by the formation of crystallographic shear planes (22). Such defects may also account for the disappearance of the expansion effect of chlorine along  $a$ -axis when  $\text{TiO}_2$  is added to  $\text{RuO}_2$ .

## 2. Electrical Conductivity

The electrical behavior of the  $\text{RuO}_2$ - $\text{TiO}_2$  coatings preheated at  $600^\circ\text{C}$  ( $\text{Ru}/\text{Cl} \approx 0.03$ ) is rather metallic in the composition range 30–100%  $\text{RuO}_2$  since the temperature coefficient of resistivity is positive for compositions above 30% and negative for lower values (Fig. 5). This conclusion supports the more recent views (8–10, 23) about the question as to whether  $\text{RuO}_2$ - $\text{TiO}_2$  mixed oxides exhibit metallic or semiconducting properties. Lodi *et al.* (23) have measured conductivities as high as  $10^3$  to  $10^4$   $\text{ohm}^{-1} \text{cm}^{-1}$  for their compact films. This means that the conductivity of  $\text{RuO}_2$  films is affected by their morphology. Grain boundaries or large quantities of chlorine (as interstitial  $\text{RuCl}_3$ -like phase for instance) may be responsible for the breakdown of the metal-like character of the  $\text{TiO}_2$ - $\text{RuO}_2$  coatings and explain the semiconducting behavior found by some authors (7, 24).

The large decrease of conductivity below 30%  $\text{RuO}_2$  (Fig. 5), was previously observed by some authors (3, 25, 26). Galyamov *et al.* (26) pointed out that the electrical conductivity of the films in the  $\text{RuO}_2$  composition range  $> 25\%$   $\text{RuO}_2$  may be regarded as the transfer (percolation) of carriers along infinite  $\text{RuO}_2$  clusters. According to Gerrard and Steele (3), the results are in agreement with the percolation theory (27) applied to a mixture of con-

ducting and insulating particles. These last authors indicate that no true solid solution exists but rather that a finely dispersed mixture of the two oxides is formed.

This situation is likely to occur in samples prepared in the absence of chlorine. From X-ray, SEM, and resistivity measurements it turns out that these samples consist of very small particles of either pure oxides or limited solid solutions. However, the above findings (3) are not reproduced here in the case of Cl-containing mixed oxides. First of all, most of the X-ray investigations tend to prove the formation of complete solid solutions, and this fact is generally accepted. Furthermore, other models may be derived, in terms of effective bonds for conductivity in the rutile lattice rather than in terms of conducting and insulating particles. The  $\text{Ru}^{4+}$  ion has a  $d^4$  electron configuration. The metallic conductivity is consistent with partial filling of the  $M$ -O  $\pi^*$  band. The  $\sigma$  Ru-Ru bonding levels parallel to  $c$ -axis are occupied so that these bonds are nonconducting (13, 28). It is reasonable to think that in pure  $\text{RuO}_2$  the metallic character is maintained along  $M$ -Cl  $\pi^*$  bands. In stoichiometric  $\text{TiO}_2$  with no  $d$  electrons, the adjacent Ti-O  $\pi^*$  and Ti-Ti  $\sigma$  bands are not filled so that these bands are separated from Ti-O  $\sigma$  and  $\pi$  valence bands by a large gap. One may assume that the  $\text{RuO}_2$ - $\text{TiO}_2$  mixed oxides form an array of resistors represented by Ru-O and Ti-O  $\pi^*$  bonds along  $\{110\}$  directions having respectively non-zero conductivity  $\sigma_1$  and conductivity  $\sigma_2 < \sigma_1 \approx 0$ . In this case, the overall conductivity falls to zero in homogeneous mixtures containing 50 at.% of each oxide. Therefore, the above assumptions do not explain the persistence of a high conductivity in the range 30–50%  $\text{RuO}_2$ . This means that either large composition heterogeneities or band overlap may occur in some crystal directions. Several arguments may be adduced for electron transport through metal-metal bonds parallel to  $c$  axis when  $\text{TiO}_2$  is introduced in the

RuO<sub>2</sub>-Cl lattice: (i) The *c/a* ratio decreases; (ii) the formal number of *d* electrons per cation decreases so that the metal-metal  $\sigma$  level would be partially filled and produce a strong Ti-Ru interaction along *c* axis; (iii) if chlorine ions are compensated by electrons localized on cationic sites, electron transport from reduced Ru<sup>3+</sup> and Ti<sup>3+</sup> ions may be possible. In addition, the *d*<sub>1</sub> configuration of Ti<sup>3+</sup> may lead to formation of metallic bonds, as previously reported by Tallan (29) in A<sup>3+</sup> TiO<sub>3</sub> perovskites. Thus, the assumption that alternative paths for electron transport exist beside conducting Ru—O  $\pi^*$  bands could explain the persistence of metallic properties in the films up to 30% RuO<sub>2</sub>, and support the existence of complete solid solutions in mixed oxide films, based on X-ray diffraction analysis.

From the present results it is believed that a fraction of the chloride ions is localized on oxygen ion sites of the rutile lattice. These ions can "open" the rutile structure by expanding the smallest parameters, i.e., *a* for RuO<sub>2</sub> and *c* for TiO<sub>2</sub>, so that solid solutions having intermediate *c/a* values can build up and exist as metastable phases at low temperature.

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