

## The Defect Structure of Rutile Containing Small Additions of Aluminium Oxide

KATRINE SEIP FØRLAND

*Institute of Inorganic Chemistry, The Technical University of Norway, Trondheim, Norway*

The defect structure of rutile ( $\text{TiO}_2$ ) containing 0.1–1 mole %  $\text{Al}_2\text{O}_3$  was studied by equilibrium measurements in the temperature region 900–1200°C and at oxygen partial pressures in the region  $10^{-8}$ – $10^{-15}$  atm.

The solubility of  $\text{Al}_2\text{O}_3$  in pure stoichiometric rutile is very small (<0.1 mole % at one atm.  $\text{O}_2$ ) but at decreased oxygen pressures  $\text{Al}_2\text{O}_3$  dissolves giving  $\text{Al}^{3+}$  ions in interstitial positions.

### I. INTRODUCTION

The defects in pure rutile at elevated temperatures consist of oxygen vacancies and electrons not associated with the vacancies.<sup>1</sup> The incorporation of foreign ions in the rutile lattice is expected to affect the equilibrium between vacancies and electrons.

Several authors have studied the effect of adding small amounts of  $\text{Al}_2\text{O}_3$  to  $\text{TiO}_2$ . Hauffe and co-authors<sup>2</sup> and Johnson<sup>3</sup> found that additions (0.5–2 %) of  $\text{Al}_2\text{O}_3$  had little effect on the electrical conductivity of  $\text{TiO}_2$ . Yahia<sup>4</sup> studied the electrical conductivity and the thermoelectric power of  $\text{TiO}_2$  with  $\text{Al}_2\text{O}_3$  (0.5 %). For decreasing oxygen pressure the conductivity went through a minimum and the thermoelectric power in contact with Pt changed sign from positive to negative. Acket and Volger<sup>5</sup> found a small effect on the Hall coefficient at very low temperatures for 100 ppm  $\text{Al}_2\text{O}_3$  in  $\text{TiO}_2$ . Haul and Dümbsgen<sup>6</sup> studied the diffusion of oxygen in  $\text{TiO}_2$  with 100–200 ppm  $\text{Al}_2\text{O}_3$ . They found no dependence on oxygen pressure and explained this by assuming that the concentration of oxygen vacancies due to the  $\text{Al}_2\text{O}_3$  content dominate over the thermally formed ones. Rao and co-authors<sup>7</sup> found that 5 at %  $\text{Al}^{3+}$  addition to pure  $\text{TiO}_2$  retarded the anatase-rutile transformation.

### II. EXPERIMENTAL

The investigation was carried out by measuring the weight changes of the samples with a thermobalance in the temperature region 900 to 1200°, and at oxygen pressures in the region  $10^{-8}$ – $10^{-15}$  atm. The experimental procedure and the thermobalance are described in detail elsewhere.<sup>1,8</sup>

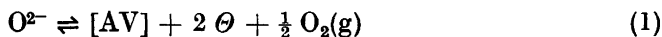
The samples were prepared by mixing pure  $\text{TiO}_2$  in the form of anatase (for analysis of  $\text{TiO}_2$ , see Ref. 1) with small amounts of  $\text{Al}_2\text{O}_3$  *p.a.* The mixtures were heated slowly to  $1400^\circ\text{C}$  at atmospheric pressure in a platinum crucible. Repeatedly the partly sintered product was cooled, crushed in an agate mortar and reheated to  $1400^\circ\text{C}$ .

After the investigation the content of  $\text{Al}_2\text{O}_3$  in each sample was determined by spectrographic analysis. It was checked that the samples contained no Pt or Zr (from sample containers).

### III. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1 shows the weight loss for samples containing different amounts of  $\text{Al}_2\text{O}_3$  at the temperatures  $1150^\circ\text{C}$  and  $1100^\circ\text{C}$ . It is seen that the weight loss is higher than for pure rutile, but of the same order of magnitude. Further it is seen that except for the sample with the lowest content of  $\text{Al}_2\text{O}_3$  (0.11 mole %  $\text{Al}_2\text{O}_3$ ) the weight loss does not depend on the amount of  $\text{Al}_2\text{O}_3$  added. At other temperatures a similar pattern was found. The weight loss was somewhat higher with  $\text{Al}_2\text{O}_3$  present, and about the same with 0.24 mole %  $\text{Al}_2\text{O}_3$  added as with 0.98 mole %  $\text{Al}_2\text{O}_3$  added.

The total weight loss is determined by at least two equilibria. One is the same as for pure  $\text{TiO}_2$ :<sup>1</sup>



$\text{O}^{2-}$  denotes an oxygen in a normal lattice position,  $[\text{AV}]$  denotes a vacant oxygen position and  $\Theta$  denotes an excess electron.

The second equilibrium must involve the aluminium. Since weight loss is independent of the amount of alumina added, the aluminium activity is

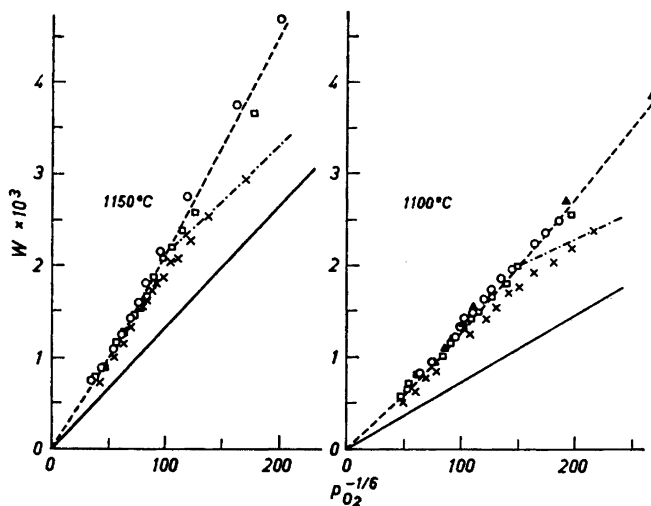


Fig. 1. Weight loss versus  $P_{\text{O}_2}^{-1/6}$  at  $1150^\circ\text{C}$  and  $1100^\circ\text{C}$ .  $W$  is weight loss calculated as molar fraction of oxygen in pure stoichiometric  $\text{TiO}_2$ .  $\times$  0.11 mole %  $\text{Al}_2\text{O}_3$ ;  $\square$  0.24 mole %  $\text{Al}_2\text{O}_3$ ;  $\blacktriangle$  0.77 mole %  $\text{Al}_2\text{O}_3$ ;  $\circ$  0.98 mole %  $\text{Al}_2\text{O}_3$ . — pure  $\text{TiO}_2$  - - -  $\text{TiO}_2$  with 0.24–0.98 mole %  $\text{Al}_2\text{O}_3$  ····  $\text{TiO}_2$  with 0.11 mole %  $\text{Al}_2\text{O}_3$ .

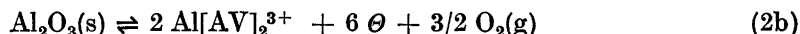
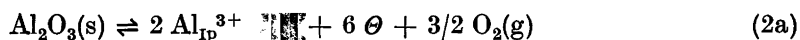
Table 1. The temperatures of the measurements ( $t^\circ\text{C}$ ), the ranges of oxygen pressures ( $P_{\text{O}_2}$ , atm.) and the logarithm of the weight loss divided by the logarithm of the oxygen pressure ( $\log W/\log P_{\text{O}_2}$ ) for the samples containing different amounts of  $\text{Al}_2\text{O}_3$ . At temperatures below  $1000^\circ\text{C}$  the measurements are inaccurate and no reliable values for  $\log W/\log P_{\text{O}_2}$  can be calculated.

0.24 mole % $\text{Al}_2\text{O}_3$			0.98 mole % $\text{Al}_2\text{O}_3$		
$t^\circ\text{C}$	$P_{\text{O}_2}$ , atm.	$\log W/\log P_{\text{O}_2}$	$t^\circ\text{C}$	$P_{\text{O}_2}$ , atm.	$\log W/\log P_{\text{O}_2}$
1002	$10^{-12.0} - 10^{-14.0}$	-1/5.47	1009	$10^{-12.0} - 10^{-14.0}$	-1/5.44
1048	$10^{-11.8} - 10^{-13.8}$	-1/5.79	1051	$10^{-11.9} - 10^{-13.9}$	-1/6.03
			1052	$10^{-12.5} - 10^{-14.6}$	-1/5.70
1100	$10^{-10.0} - 10^{-13.8}$	-1/5.62	1095	$10^{-10.9} - 10^{-13.6}$	-1/5.58
1149	$10^{-9.1} - 10^{-13.5}$	-1/5.54	1152	$10^{-10.0} - 10^{-13.8}$	-1/5.33
1184	$10^{-8.9} - 10^{-12.0}$	-1/5.44	1200	$10^{-8.4} - 10^{-12.0}$	-1/5.49
0.77 mole % $\text{Al}_2\text{O}_3$					
1105	$10^{-11.8} - 10^{-14.6}$	-1/5.57			
1200	$10^{-10.8} - 10^{-14.0}$	-1/5.65			

constant and the reaction is heterogeneous (except for the sample containing 0.11 mole %  $\text{Al}_2\text{O}_3$  which is discussed at the end of this paper). Since the weight loss is of the same order of magnitude as for the pure rutile, no one of the reactions is expected to predominate over the other.

The weight loss for the pure rutile is proportional to  $P_{\text{O}_2}^{-1/6}$ . Table 1 shows that the weight loss for the  $\text{Al}_2\text{O}_3$  containing rutile is proportional to  $P_{\text{O}_2}^{-1/a}$  where  $a$  is a number between 5 and 6. The weight loss represents the added effects of two reactions. If no anion vacancies or quasifree electrons be formed by the second reaction, the two reactions would be independent of each other. In such a case  $a$  may be calculated for the second reaction after subtracting the weight loss for pure rutile. For the  $\text{TiO}_2$  with 0.24 mole %  $\text{Al}_2\text{O}_3$  the value of  $a$  will be 5 at  $1100^\circ\text{C}$ . If there is interaction between the two reactions, the value of  $a$  is higher ("common ion effect"). From this is concluded that the second reaction gives between 5 and 6 particles in the lattice for each  $\text{O}_2(\text{g})$  formed.

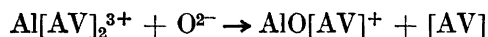
Equilibria which fit well with the experimental results are



$\text{Al}_{\text{ip}}^{3+}$  denotes an  $\text{Al}^{3+}$  in an interstitial position,  $\text{Al}[\text{AV}]_2^{3+}$  denotes an  $\text{Al}^{3+}$  in a  $\text{Ti}^{4+}$  lattice position associated with two anion vacancies.

According to the phase diagram for  $\text{Al}_2\text{O}_3-\text{TiO}_2$ ,<sup>9</sup> the separate phase in equilibrium with pure rutile is not  $\text{Al}_2\text{O}_3$  but  $\beta\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ . The above way of writing is chosen for simplicity.

Hurlen<sup>10</sup> has pointed out that there are interstitial positions in the rutile lattice large enough to accommodate  $\text{Al}^{3+}$  ions. Both reactions give 5.3 particles in the lattice for each  $\text{O}_2(\text{g})$  formed, and the experimental results do not give any basis for a preference between these two possibilities. Reaction 2 b, however, with a cluster of three associated defects seems unlikely from an energetic point of view. The dissociation of the particle



would give a more even distribution of electrical charges, but to fit the experimental results no significant dissociation could be allowed. Eqn. 2 a is therefore adopted together with eqn. 1 for further calculations.

The equilibrium constant for eqn. 1:

$$K_{\text{I}} = N_{[\text{AV}]} \cdot N_{\theta^2} \cdot P_{\text{O}_2}^{+1/2} / N_{\text{O}^{2-}} \quad (\text{I})$$

where  $N$  with index denotes concentration (number of particles divided by number of regular oxygen positions). For small concentrations of defects  $N_{\text{O}^{2-}} \approx 1$ . The equilibrium constant for eqn. 2 a:

$$K_{\text{II}} = N_{\text{Al}^{3+}} \cdot N_{\theta^6} \cdot P_{\text{O}_2}^{3/4} \quad (\text{II})$$

( $N_{\text{Al}^{3+}}$  denotes  $\text{Al}^{3+}$  in interstitial positions).

The measured weight loss,  $W$ , calculated as a fraction of the oxygen in pure stoichiometric  $\text{TiO}_2$ :

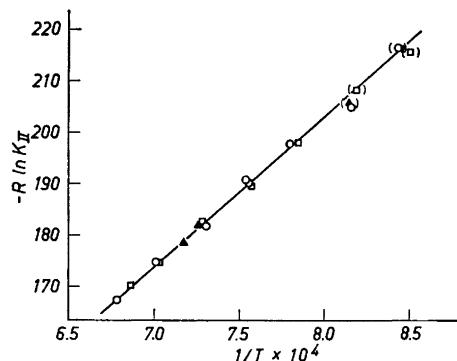
$$W = \frac{1}{2} N_{\theta} = N_{[\text{AV}]} + 3/2 N_{\text{Al}^{3+}} \quad (\text{III})$$

The values of  $K_{\text{I}}$  for each temperature are known<sup>1</sup> and by means of eqns. (I), (II), and (III)  $K_{\text{II}}$  can be calculated from the weight losses at the different temperatures and oxygen pressures. The change in enthalpy for a reaction may be determined from the equations

Table 2. The Gibbs free energy for eqn. 2 a divided by the absolute temperature ( $-R \ln K_{\text{II}}$ ) at the different temperatures of measurement ( $t^\circ\text{C}$ ).

0.24 mole % $\text{Al}_2\text{O}_3$		0.77 mole % $\text{Al}_2\text{O}_3$		0.98 mole % $\text{Al}_2\text{O}_3$	
$t^\circ\text{C}$	$-R \ln K_{\text{II}}$	$t^\circ\text{C}$	$-R \ln K_{\text{II}}$	$t^\circ\text{C}$	$-R \ln K_{\text{II}}$
902	215.6	953	205.4	912	216.5
948	208.3			952	205.0
1002	198.1			1002	197.8
1048	189.6			1051	190.4
1100	182.6	1105	181.8	1052	190.9
				1095	181.8
				1149	175.0
				1120	178.4
1184	170.2	1152	174.1	1200	167.3

Fig. 2.  $-R \ln K_{II}$  versus  $1/T \times 10^4$ .  $\square$  0.24 mole %  $\text{Al}_2\text{O}_3$ ;  $\blacktriangle$  0.77 mole %  $\text{Al}_2\text{O}_3$ ;  $\circ$  0.98 mole %  $\text{Al}_2\text{O}_3$ .



$$\Delta G^\circ = -RT \ln K$$

$$\text{and } \partial \left( \frac{\Delta G^\circ}{T} \right) / \partial \left( \frac{1}{T} \right)_P = \Delta H^\circ$$

In Table 2 the values of  $-R \ln K_{II}$  for the different series of measurements are given, and in Fig. 2  $-R \ln K_{II}$  is plotted as a function of  $1/T$ . The slope of the line in the figure gives the change in enthalpy for reaction 2,  $\Delta H^\circ = 293$  kcal.

From Fig. 1 it was seen that the sample containing 0.11 mole %  $\text{Al}_2\text{O}_3$  has a smaller weight loss than the samples containing more  $\text{Al}_2\text{O}_3$ . The dashed lines represent the total weight loss caused by reactions 1 and 2 as calculated from the constants  $K_I$  and  $K_{II}$  at the given temperatures. The dash-dot lines represent the curves which would be obtained for a sample containing 0.11 %  $\text{Al}_2\text{O}_3$  when  $\text{Al}_2\text{O}_3$  is insoluble in pure stoichiometric  $\text{TiO}_2$ . The experimental values do not fit the curves completely. This indicates a small solubility of  $\text{Al}_2\text{O}_3$  in  $\text{TiO}_2$ . Below a certain oxygen pressure there is no more left of the separate phase containing  $\text{Al}_2\text{O}_3$  and the equilibrium is no longer described by the heterogeneous reaction 2 a. The measurements are not accurate enough to allow conclusions about how  $\text{Al}_2\text{O}_3$  dissolves in stoichiometric  $\text{TiO}_2$  or how much, but the measurements indicate that the solubility is less than 0.1 mole %  $\text{Al}_2\text{O}_3$  in stoichiometric  $\text{TiO}_2$ .

*Acknowledgement.* The author is indebted to *Norges Teknisk-Naturvitenskapelige Forskningsråd* for financial support, to Titan Co. A/S who furnished the sample of titanium dioxide, and to Mr. Torbjørn Eliassen for carrying out experimental measurements.

#### REFERENCES

1. Førland, K. S. *Acta Chem. Scand.* **18** (1964) 1267.
2. Hauffe, K., Grunewald, H. and Tränckler-Greese, R. *Z. Elektrochem.* **56** (1952) 937.
3. Johnson, G. H. *J. Am. Ceram. Soc.* **36** (1953) 97.
4. Yahia, J. *Phys. Rev.* **130** (1963) 1711.
5. Acket, G. A. and Volger, J. *Physica* **30** (1964) 1667.

6. Haul, R. and Dümbgen, G. *J. Phys. Chem. Solids* **26** (1965) 1.
7. Rao, C.N.R., Turner, A. and Honig, J. M. *J. Phys. Chem. Solids* **11** (1959) 173.
8. Førland, K. S. and Førland, T. *Kgl. Norske Videnskab. Selskabs, Forh.* **38** (1965) No. 18.
9. Lang, S. M., Fillmore, C. L. and Maxwell, L. H. *J. Res. Natl. Bur. Std.* **48** (1952) 301.
10. Hurlen, T. *Acta Chem. Scand.* **13** (1959) 365.

Received April 29, 1966.