

Growth of titanium oxide overlayers by thermal oxidation of titanium

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This paper describes a theoretical model for the growth of titanium oxide by thermal oxidation of titanium. It is shown that this model can explain the formation of layers of different oxides of titanium and the changes in these layers with variations in the conditions of oxidation. Some experimental X-ray diffraction results which support the model are also given.

1. Introduction

Titanium oxide has been studied extensively in the last few decades [1-10] from the point of different methods of preparation, the stoichiometry of the oxide, its layered structure and its growth kinetics. When the oxide is prepared by a thermal oxidation process, it has generally been observed that it has a layered structure consisting of TiO₂, Ti₂O₃, TiO, titanium, etc. [6, 7] from the surface to the metal-oxide interface. However, no quantitative estimates have been provided to determine the variations in the percentage of the various stable oxides across the thickness. It is also reported that the composition of the layer changes with changes in the method of preparation [9, 10]. In this paper, the authors propose a model for the growth of titanium oxide by thermal oxidation which enables an estimation of the various oxides present in the oxide layer for different conditions of growth to be made. The following sections describe in detail the model and the results of computations based on it.

2. Model for growth of titanium oxide

When a fresh titanium surface is exposed to an oxygen atmosphere oxygen is absorbed in the titanium and, with passage of time, lower oxides of titanium are expected to form in the first instance. As time progresses further, oxygen has to pass through this initial oxide layer in order to reach the titanium oxide-titanium interface and form fresh oxide. As it passes through the lower oxide, some of the oxygen is expected to be absorbed by the oxide which is converted into a higher oxide and the remainder is expected to reach the titanium oxide-titanium interface. In view of these possible processes, an analysis of the oxygen transport and the formation of oxide is carried out as shown below.

3. Analysis

Assuming that oxygen transport through the oxide layer is by diffusion, at any time t the amount of oxygen trapped per unit time in a small layer, dx , located at a distance x from the surface of the oxide layer can be expressed as

$$Q_T = A dJ \quad (1)$$

where A is the area and dJ is the change in the rate of flow of oxygen across dx . This trapped oxygen is utilized to increase the free oxygen concentration as well as for the conversion of lower oxides to higher oxides.

The rate of change of free oxygen atoms in dx is given by

$$Q_F = A dx \frac{dN(x, t)}{dt} \quad (2)$$

where N is the number density of free oxygen atoms.

It is assumed that the rate of change in the number of oxygen atoms chemically absorbed in the oxide for conversion of lower oxides to higher oxides depends on the number of free oxygen atoms (N) available and the number of vacancies available in the oxide for accepting these atoms. In titanium oxide, the highest oxide possible is TiO₂. It is assumed that the oxide can in general be represented as TiO _{I} , where I can take values from 0 to 2. Therefore, the deviation of I from 2 indicates the vacancies available in the oxide for absorbing free oxygen. In view of this, the rate of change in the number of oxygen atoms chemically absorbed can be expressed as

$$Q_A = Kn_0 N(2 - I) A dx \quad (3)$$

where n_0 is the number of titanium atoms per unit volume and K is a constant of proportionality. Combining Equations 1, 2 and 3 one gets

$$-A dJ = A dx \frac{dN(x, t)}{dt} + A dx C N \xi(x, t) \quad (4)$$

where $C = Kn_0$ and $\xi(x, t) = 2 - I(x, t)$.

Rewriting Equation 4 and realising that $J = -D(dN/dx)$, one gets

$$D \frac{d^2N}{dx^2} = \frac{dN}{dt} + CN \xi(x, t)$$

or

$$\frac{\partial N(x, t)}{\partial t} = D \frac{\partial^2 N(x, t)}{\partial x^2} - CN(x, t) \xi(x, t) \quad (5)$$

where D is the diffusion coefficient of oxygen. Further, I may be expressed as a function of time by assuming

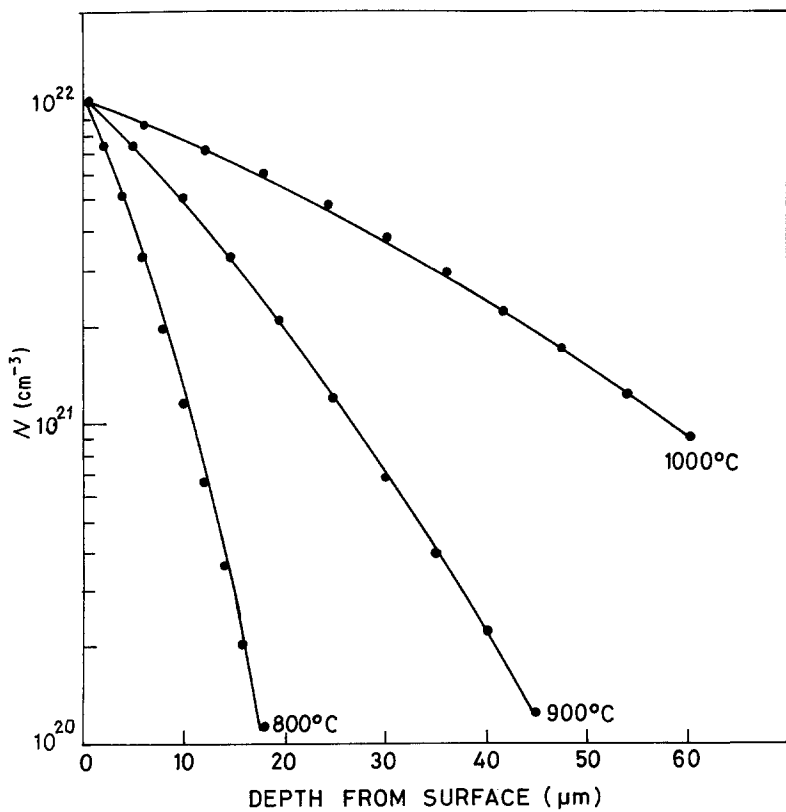


Figure 1 Computed variations in free oxygen concentrations with depth at different temperatures.

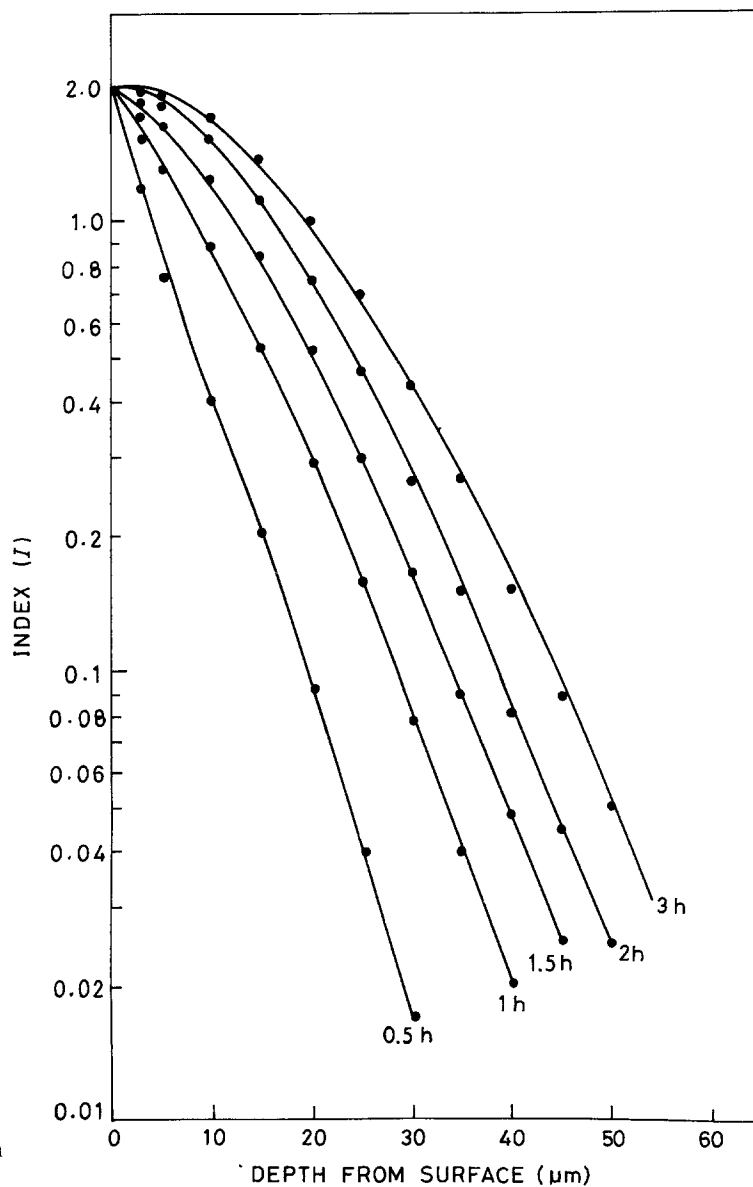


Figure 2 Computed variations in the index I with depth for different time durations at 900°C.

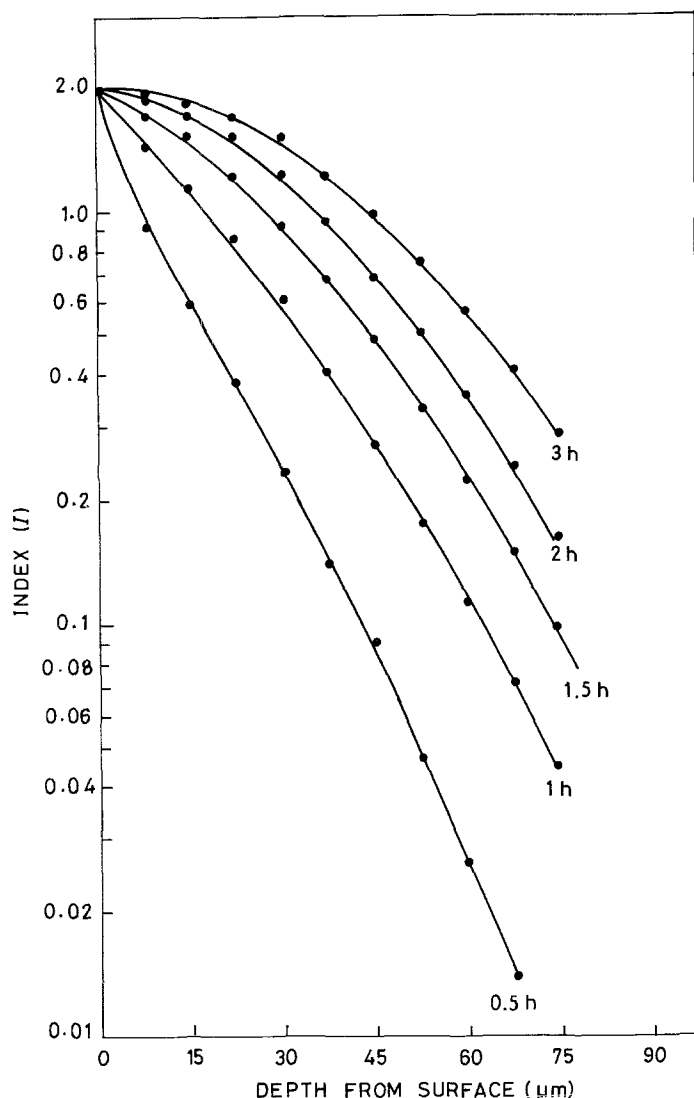


Figure 3 Computed variations in the index I with depth for different time durations at 1000°C .

that the oxygen chemically absorbed is equally distributed between all the titanium atoms, that is

$$\frac{\partial I(x, t)}{\partial t} = \frac{CN(x, t)}{n_0} \quad (6)$$

The differential Equations 5 and 6 may be solved together with the following boundary conditions:

- (i) The number of free oxygen atoms per unit volume at the surface is N_0 for all values of t .
- (ii) At $t = 0$, $N(x, t)$ within the oxide layer is zero (neglecting the oxygen dissolved initially in titanium).

The solutions have been obtained by numerical methods for different values of C , taking appropriate values of D at different temperatures.

The solutions give the variations in N and I with respect to distance (x) and time (t) for different temperatures of oxidation. Typical variations are shown in Figs 1 to 3.

4. Formation of stable oxides

From the results of the analysis given above (Figs 2 and 3), it may be seen that the index I in TiO_7 varies with depth continuously from the surface of the oxide down to the titanium metal. However, in practice, TiO_7 in any layer of the oxide consists of a few stable oxides, namely TiO_2 , Ti_2O_5 , Ti_2O_3 , TiO and Ti_2O which combine in appropriate proportions so that the

stoichiometry corresponds to the I value for that layer. In view of this, an attempt has been made to determine the percentages of these oxides formed in different layers of the oxide using the I values for the layers. For this purpose, assuming that an aggregate of 10 titanium atoms and an appropriate number of oxygen atoms, corresponding to the stoichiometry TiO_7 , forms a basic unit which might be considered to be repeated throughout the oxide at that depth, the various possible combinations of the different oxides have been formulated. Assuming that all these combinations are equally probable, the proportion of a particular oxide will be proportional to the total number of molecules of that particular oxide in the total number of combinations times the basic unit corresponding to TiO_7 . On these lines, the percentage compositions of all the oxides at any given depth can be obtained. In this, it has been assumed that no free titanium exists with other oxides except with Ti_2O .

5. Results and discussion

Based on this method of estimation, the variation in the percentage composition of the various oxides across the depth of the titanium oxide layer has been computed for different values of the temperature of oxidation. Typical variations are shown in Figs 4 to 6. From the same calculations, the variations in the percentages of the different oxides with time of oxidation

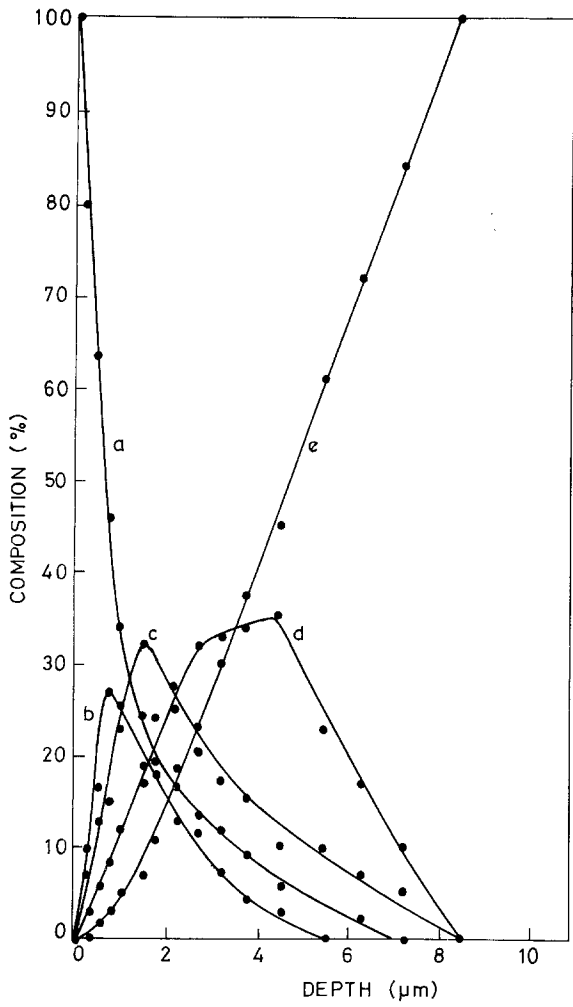


Figure 4 Variations in composition for different oxides with depth for a duration of 0.5 h at 900°C: (a) TiO_2 , (b) Ti_3O_5 , (c) Ti_2O_3 , (d) TiO , (e) Ti_2O .

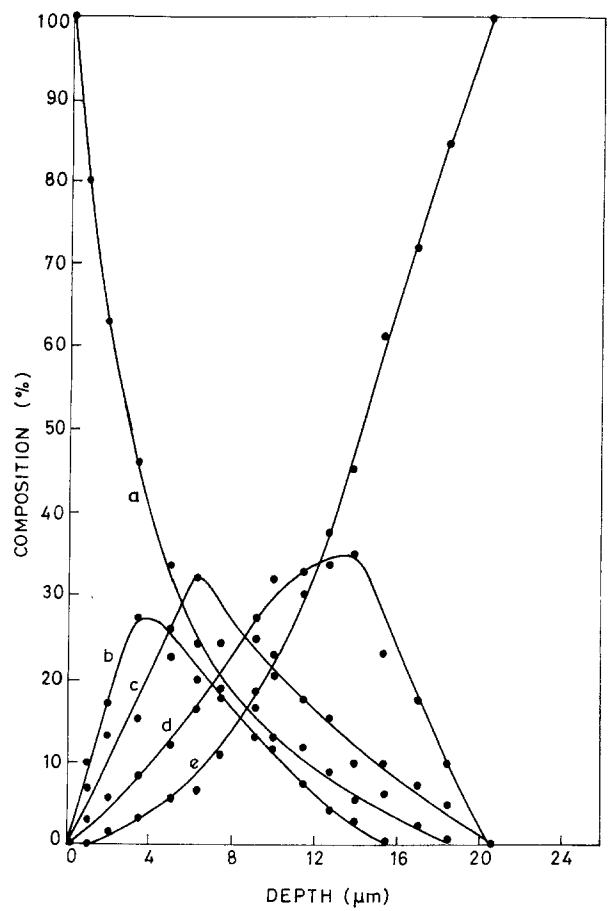


Figure 5 Variations in composition for different oxides with depth for a duration of 1.5 h at 900°C: (a) TiO_2 , (b) Ti_3O_5 , (c) Ti_2O_3 , (d) TiO , (e) Ti_2O .

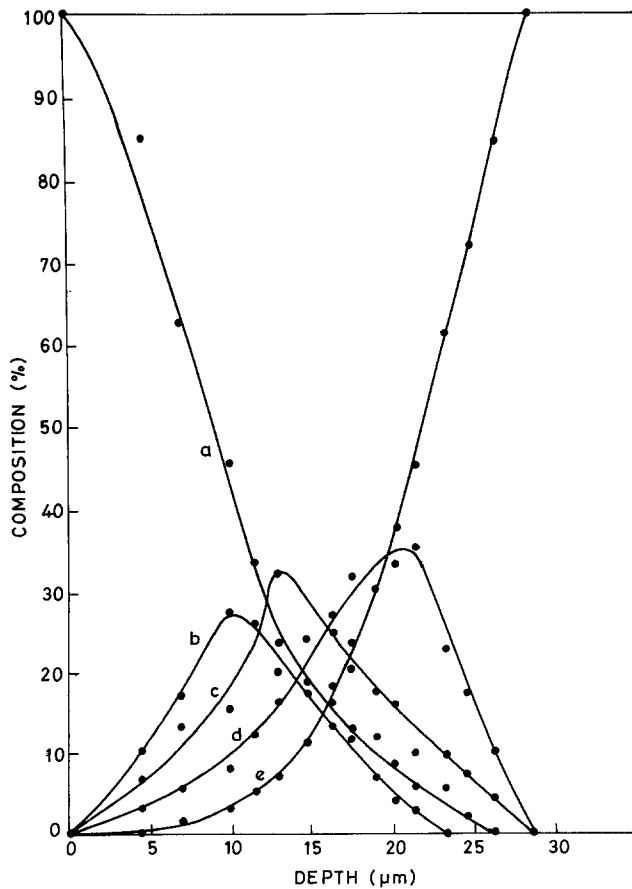


Figure 6 Variations in composition for different oxides with depth for a duration of 3 h at 900°C: (a) TiO_2 , (b) Ti_3O_5 , (c) Ti_2O_3 , (d) TiO , (e) Ti_2O .

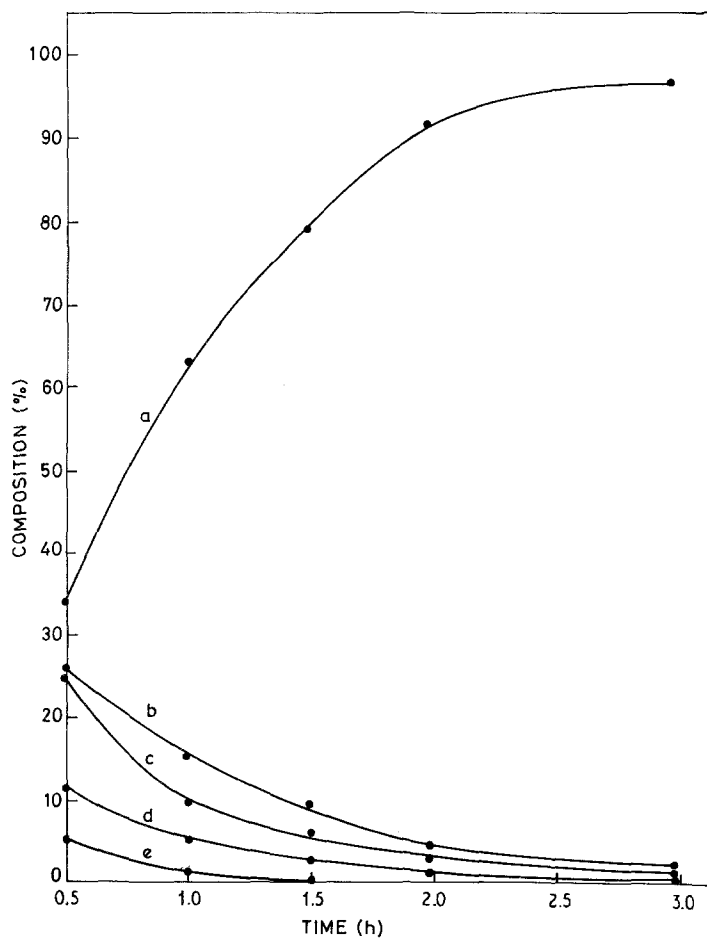


Figure 7 Variations in composition for different oxides with time at 900°C at a depth of 1 μm: (a) TiO₂, (b) Ti₃O₅, (c) Ti₂O₃, (d) TiO, (e) Ti₂O.

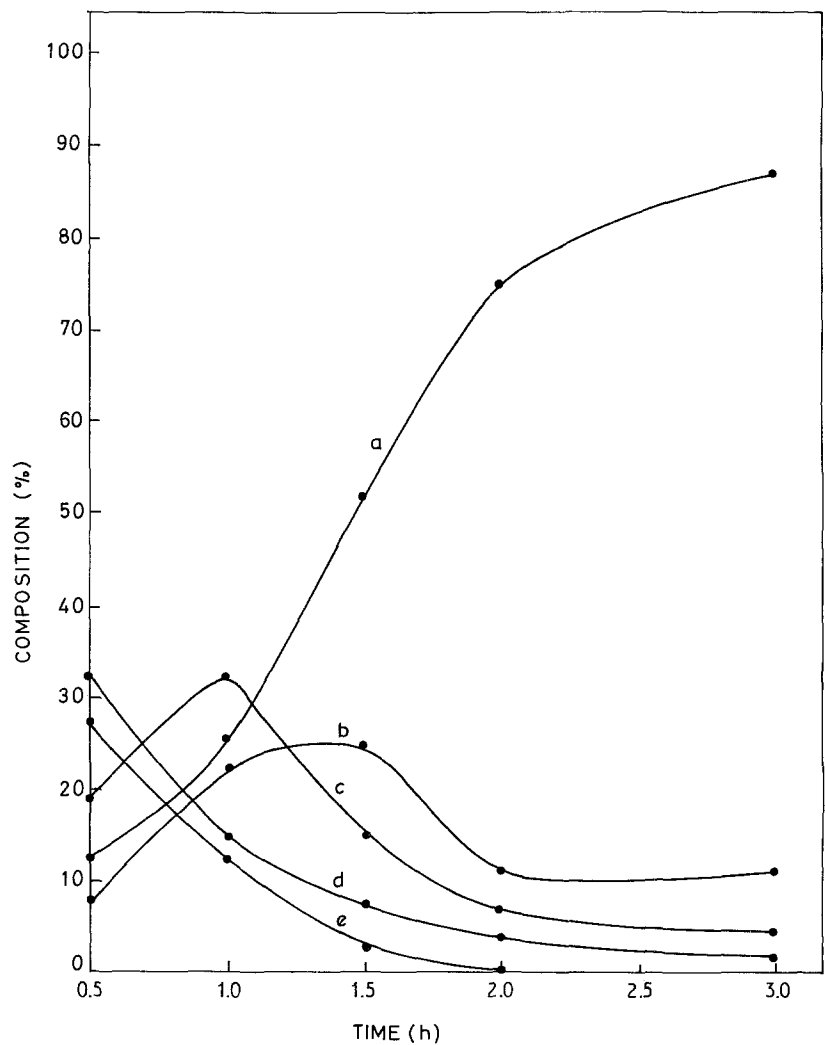


Figure 8 Variations in composition for different oxides with time at 900°C at a depth of 3 μm: (a) TiO₂, (b) Ti₃O₅, (c) Ti₂O₃, (d) TiO, (e) Ti₂O.

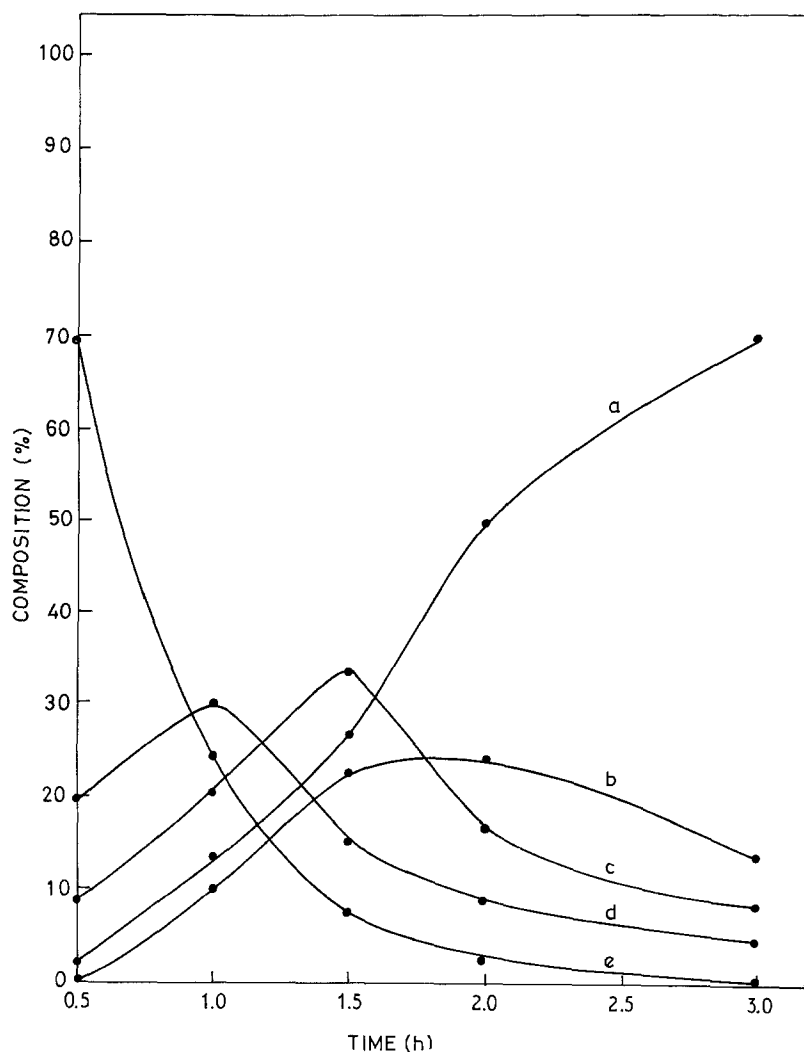


Figure 9 Variations in composition for different oxides with time at 900°C at a depth of 6 μm: (a) TiO₂, (b) Ti₃O₅, (c) Ti₂O₃, (d) TiO, (e) Ti₂O.

at different depths have also been obtained. Typical variations are shown in Figs 7 to 9.

From Figs 4 to 6, it may be seen that the percentage of TiO₂ is the highest on the surface of the oxide and gradually decreases to a minimum near the oxide-metal interface. The percentage of Ti₂O is lowest at the surface and gradually increases to a maximum at the oxide-metal interface. The other intermediate oxides show maximum values somewhere in the middle of the

oxide layer in the order Ti₃O₅, Ti₂O₃, TiO. Furthermore, it may be seen that there are regions of the oxide where a particular oxide dominates over the other oxides. Because of this, it may be realized that the oxide has a layered structure.

From Figs 7 to 9, it may be seen that TiO₂ at any particular depth increases with time whereas Ti₂O decreases with time and the other oxides first increase with time and then decrease, showing a maximum at

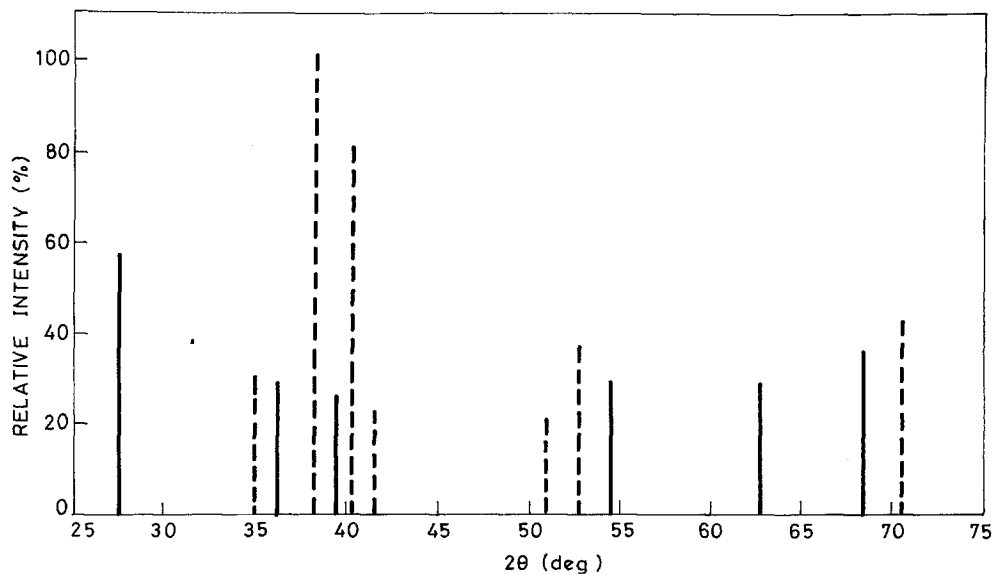


Figure 10 X-ray diffraction pattern for titanium oxide sample oxidized at 700°C for 1 h: (—) TiO₂, (---) other oxides.

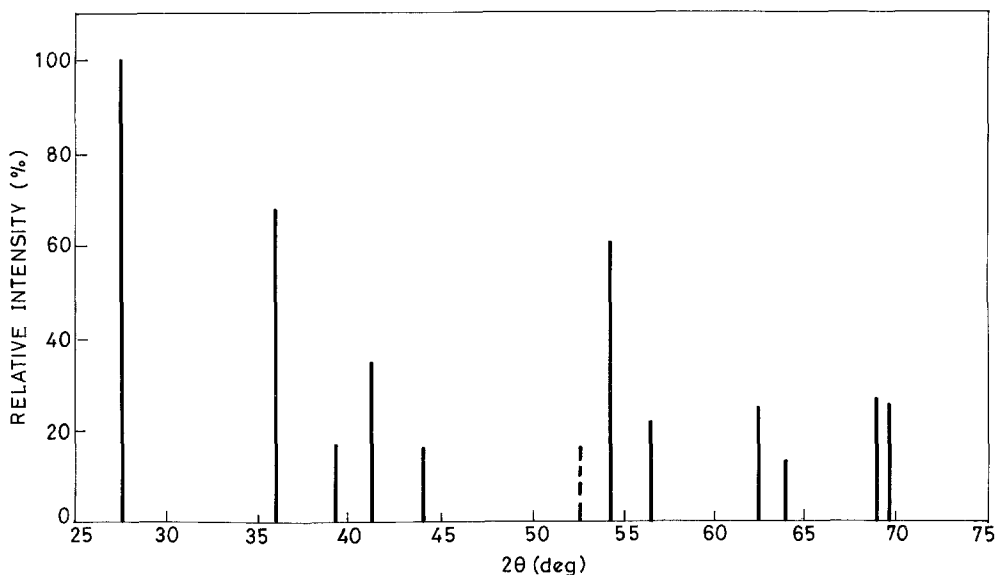


Figure 11 X-ray diffraction pattern for titanium oxide sample oxidized at 900°C for 4 h: (—) TiO₂, (---) other oxides.

a particular time. Thus, it may be concluded that the oxides start growing at different depths at different points of time.

Computations carried out at different temperatures of oxidation have also indicated the same structure for the oxide. Also, calculations using different sizes of the basic unit have yielded similar results.

Thus, it may be seen from this analysis that oxides prepared for short periods of time or at low temperatures show a large number of oxides of titanium on the surface, which gradually become transformed to TiO₂ with time. To verify these results, titanium oxide layers thermally grown at different temperatures and time durations have been subjected to X-ray diffraction analysis. Typical diffractograms are shown in Figs 10 and 11. These studies showed that the oxides prepared for longer periods or at higher temperatures contain only rutile (TiO₂) at the surface, while those prepared at low temperatures and for shorter durations show all the oxides.

6. Conclusions

The analysis of the growth of titanium oxide described above clearly indicates that the oxide has a layered structure, and that these layers contain different oxides in various proportions. The top layers are rich in TiO₂ but layers deeper inside contain other oxides. With increase in either temperature or time of oxida-

tion, more and more layers from the surface become rich in TiO₂ of the rutile type. Thus, it may be concluded that the model proposed in this paper explains the layered structure of the titanium oxide grown by thermal oxidation as reported by Morton *et al.* [6], David *et al.* [7] and others.

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