

Effect of Oxygen Activity on Niobium Segregation in Niobium-Doped Titanium Dioxide

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Abstract

The present paper considers the effect of segregation of niobium in polycrystalline, Nb-doped titanium dioxide, Nb-TiO₂. Specifically, the effect of oxygen activity, controlled during processing, on segregation is investigated. It was observed that Nb segregation is favoured by low oxygen activity, especially when the Nb dopant concentration is less than 3 at %. This is interpreted in terms of the defect equilibria that describe Nb incorporation. While it is not considered that the present data reflect equilibrium segregation, it is considered that the observed behaviour is tending towards the equilibrium case, and so the applied interpretation is valid. From these results it is clear that segregation may be controlled in order to impose desired functional properties in advanced materials such as TiO₂ for solar driven water splitting.

Keywords: Titanium dioxide, niobium, segregation, calibration, photo-catalysis

INTRODUCTION

The surface properties of ionic solids, such as chemical composition, structure and the related semiconducting properties can be entirely different from those of the bulk phase [1]. It is often the case that the nature of the surfaces or interfaces can greatly influence or even determine the functional properties exhibited by a particular material. This is frequently the case in polycrystalline materials where the presence of a grain boundary phase can dictate the properties exhibited, and consequently, the scope for application. Hence, it is important that both the properties of the surface/interface and the bulk phase are considered during the processing of advanced materials.

In recent times, titanium dioxide, TiO₂, has been the focus of intense research world wide due to its potential for applications in areas such as energy conversion [2,3,4,5,6], water purification [7], and self-cleaning and superhydrophilic surfaces [8]. Much of this focus originated with the discovery by Fujishima and Honda [2] in 1972, which demonstrated that water could be photo-electrochemically split using TiO₂ photo-anodes. This provided promise for the replacement of fossil fuels with a sustainable alternative; hydrogen. Unfortunately, a commercially viable photo-

electrode based on TiO₂ has not yet been developed. This is largely due to an inability to suitably address a number of key issues relating to the function of TiO₂ during the water splitting process. Related to several of these key issues, a thorough understanding of how the surface properties of TiO₂ may be manipulated would contribute significantly towards the development of an efficient TiO₂ photo-electrode.

In the present paper, the segregation of Nb to the surface of polycrystalline Nb-doped TiO₂ is considered following processing that is well defined by temperature and oxygen activity. The aim of the paper is to demonstrate that the processing of TiO₂ can have a strong bearing on the surface properties, in particular, the surface chemical composition. The potential consequences relating to photo-electrochemical water splitting are discussed.

SEGREGATION AND ITS EFFECT ON PHOTO-ELECTROCHEMICAL WATER SPLITTING

Segregation is a mass transport process in which point defects migrate towards surfaces and interfaces under the driving force of free energy minimization [9,10]. This migration leads to the enrichment of surface and interfaces in these migrating point defects, such as impurity cations, resulting in the formation of a concentration gradient that extends from the surface/interface inwards towards the bulk of the solid. This concentration gradient also induces an electric field whose polarization depends upon the specific defects that have segregated. This phenomena has been schematically illustrated in Fig 1. This figure also indicates that an electric field as strong as 10^5 Vcm^{-1} is possible when the enrichment factor (ratio of surface concentration to bulk concentration) reaches 100. Naturally, segregation can only occur when ions are able to migrate, which is at elevated temperatures in the case of ionic solids such as TiO_2 .

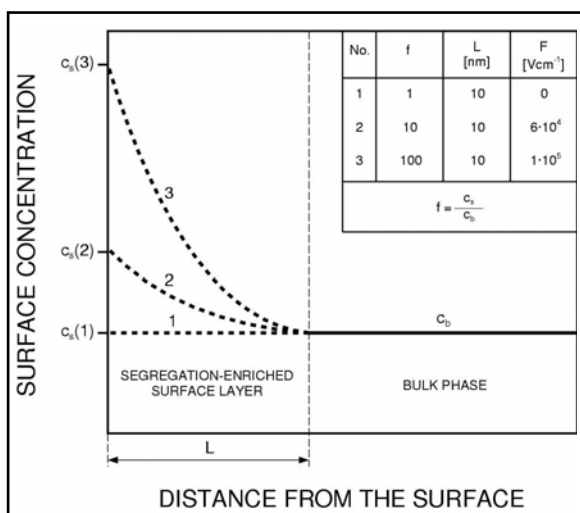


Fig. 1: Schematic illustration of surface segregation, and the associated electric fields

Nowotny et al [11] have outlined the key parameters that must be addressed, and suitably optimized in order to develop an efficient photo-electrode for photo-electrochemical water splitting. The modification of surface and interface properties can assist in the optimization of some of these functional properties, as outlined below:

- *Charge transfer*

The splitting of water requires that electronic charge must be exchanged between the photo-electrode material (TiO_2) and adsorbed water molecules. The surface chemical composition must be made suitable for efficient charge transfer to occur. This may involve the imposition of specific surface active sites, such as titanium vacancies, which can

effectively accept electrons from water molecules promoting them to split. Alternatively, segregation-induced electric fields may be imposed to promote electronic charge transfer in a desired direction.

- *Charge transport*

Grain boundaries provide a continuous route for charge transport through a polycrystalline solid. Consequently, the presence of a highly conducting or highly insulating grain boundary phase can completely dictate the transport of charge through a photo-electrode. In this case, both the tendency for grain boundary segregation to occur under given processing conditions, and the manner in which these may be manipulated in order to maximize charge transport must be assessed.

- *Flatband potential*

The flatband potential provides both the driving force for the water splitting reaction and ensures efficient charge separation. The imposition of suitably oriented segregation-induced electric fields can provide additional potential to assist in serving these two important functions.

In summary, segregation has substantial significance with respect to photo-electrochemical water splitting. Furthermore, segregation can clearly be used as tool for imposing the desired key functional properties. However, the need for understanding how segregation can be controlled through processing is pertinent.

REVIEW OF LITERATURE

The literature reporting segregation of various cations in TiO_2 has been recently reviewed by Nakajima et al [10]. This review highlighted the need to ensure that segregation is studied under well defined processing conditions. This means that during processing, both temperature and oxygen activity must be controlled. Furthermore, literature reports fail to provide any evidence for the attainment of equilibrium segregation. This is a critical omission, as it is important to be able to identify whether the segregation behaviour observed is indicative of thermodynamic conditions, or is indicative of a kinetic process in which the observed behaviour is but a snapshot of a greater process. Equilibrium segregation data is needed in order to use segregation as a tool for imposing desirable functional properties. However, it is difficult to ensure that equilibrium has been achieved due to the absence of well defined kinetic data, which have never been reported for segregation in TiO_2 .

In addition to controlling temperature and oxygen activity during processing, microstructure has also been shown to be an important point of consideration. Terwilliger and Chiang [12,13] have

demonstrated that grain size can strongly influence the observed segregation behaviour. For Ca segregation in Ca-doped TiO₂, these researchers found that a critical grain size of 150 - 350 nm exists, which, when exceeded results in the exsolution of CaTiO₃ during the investigated processing conditions. For grain sizes of less than 50 nm, it was found that the bulk may become completely devoid of Ca. Hence, this study has provided evidence for the ability of grain boundaries to dissolve Ca. This conclusion is somewhat complicated by the competing kinetics of grain boundary migration and segregation during processing at elevated temperatures, but demonstrates the need to study microstructural influences on segregation.

EXPERIMENTAL PROCEDURE

Preparation of Specimens

Nb-doped TiO₂ powders were prepared by the sol-gel method from the hydrolysis of Ti-isopropoxide (97% - Aldrich) mixed with sufficient NbCl₅ (99% - Aldrich) to precipitate doped TiO₂ powders. Mixtures of ti-isopropoxide, ethanol and NbCl₅ were combined and stirred at room temperature, before being gently heated to 373 K, until the mixture became no longer fluid. The temperature was then increased to 383 K and the mixture was left to fully dry, producing the doped powder. The powders were then calcined at 900°C for 2.5 hours under an oxygen atmosphere, after which they were uniaxially dry pressed to approximately 40 MPa, before cold isotatic pressing to 400MPa. The pellets were then sintered at 1773 K in air for 5 hours. After sintering, the specimens were polished to a high mirror finish. Surface analysis was initially performed on the as-polished surfaces to establish the bulk yields. Afterwards, the specimens were re-polished, annealed at 1273 K for 20h in different conditions of oxygen activity and analysed again to establish the effect of processing on the surface concentration profile.

Chemical Analysis

To accurately establish the bulk Nb content in the specimens, ion-coupled plasma mass spectrometry (ICP/MS - Perkin Elmer Elan 6000) was used. This was performed on a small sample of each of the calcined powders, which were firstly dissolved in a 1:1 mixture of lithium metaborate and lithium tetraborate powders in a platinum crucible at 1373 K for 1 hour. Once cool, the fused samples were removed from the crucible and dissolved in a solution of concentrated HNO₃, HF and distilled water. The solutions were then analyzed using ICP/MS.

Surface Analysis

Surface analysis was performed using SIMS (Cameca IMS-5f). The primary ion beam consisted of Cs⁺ ions with a net impact energy of 3keV and a raster area of 250µm x 250µm. Typical ion beam currents ranged from 10 nA to 32 nA. In order to reduce the possibility of 'edge effects', aperture and lens settings were applied to only admit positive secondary ions into the mass spectrometer from a circular area of 55µm diameter within the rastered region. The instrument was operated at a working pressure of 10⁻⁹ Torr with a mass resolution of M/ΔM ~300 and energy bandpass of 130eV. To minimise surface charging, the specimens were coated with gold (5-10nm thick). After sputtering, the crater depth was determined from the average of several surface profiles obtained using a profilometer (Dektak Alpha Step). The gold coating was not removed prior to profilometry since it helped to identify the SIMS craters. The gold coating was removed prior to each annealing treatment using warm (~323 K) *aqua regia*.

RESULTS AND DISCUSSION

In order to quantitatively assess data obtained using SIMS, a concentration and depth calibration must be made using suitable reference specimens. This issue has been recently assessed by the author [14] with the obtained concentration calibration plot available elsewhere [14]. This important result was obtained using the same specimens as the present work, and so is completely suitable for use in the present quantitative assessment of Nb segregation in Nb-doped TiO₂.

The effect of oxygen activity ($p(O_2)$) on Nb concentration profiles for 0.65 at % Nb-doped TiO₂ are displayed in Fig 2. It is clear from this figure that the observed segregation behaviour is promoted by lowered $p(O_2)$. For processing in $p(O_2)$ equal to 10 Pa, surface Nb enrichment was a factor of 13.1 over the bulk Nb concentration, while at $p(O_2)$ equal to 21 kPa, the enrichment factor was substantially less at 7.6.

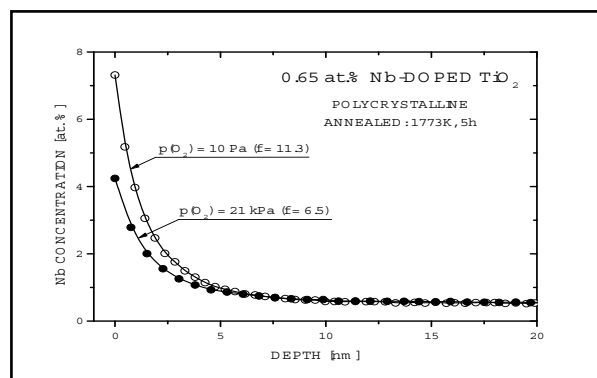
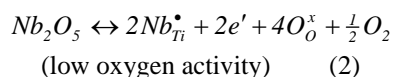
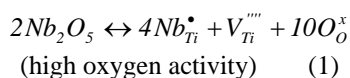


Fig. 2: Effect of oxygen activity on Nb segregation for 0.65 at. % Nb-doped TiO₂

The incorporation of Nb into the TiO₂ lattice can be considered in terms of defect disorder equilibria such as:



whose predominance is determined by the equilibrium $p(\text{O}_2)$. This defect disorder has recently been considered by Sheppard et al [15] for 0.65 at % Nb-doped TiO₂. It was found that at 1298 K (the maximum temperature investigated), the defect disorder described by Equation 1 predominates for $p(\text{O}_2) > 10$ Pa. However, with increased temperature, this critical oxygen activity was also observed to increase. Hence, through extrapolation to 1773 K, the two segregation profiles displayed in Figure 3 can be considered to correspond to the two possible incorporation mechanisms; the profile obtained at high $p(\text{O}_2)$ corresponding to Eqn 1, and the profile obtained at low $p(\text{O}_2)$ corresponding to Eqn 2.

The results reported by Sheppard et al [15] were obtained under equilibrium conditions. In the present case, it is uncertain whether the segregation behaviour observed similarly represents equilibrium. However, the tendency to achieve equilibrium is certain. Hence, it can be concluded that at high oxygen activity, segregation kinetics are slower than at low oxygen activity. Considering the defect disorder involved, this is most likely due to the need for slow ionic transport at high $p(\text{O}_2)$ (titanium vacancy migration) compared to rapid electronic transport (electron migration) at low $p(\text{O}_2)$. This would require verification by assessing the change in the observed segregation profiles as a function of processing time.

The effect of oxygen activity on the enrichment factor as a function of Nb bulk concentration is displayed in Fig 3. Whilst displaying a $p(\text{O}_2)$ independence for bulk concentrations greater than 3 at % Nb, at lower concentrations a clear effect of $p(\text{O}_2)$ is observed. This effect is consistent discussed model which favours Nb segregation at low oxygen activity. It could be speculated that for Nb bulk concentrations beyond 3 at %, both segregation profiles are defined by the same defect equilibria, and hence display only minor profile differences.

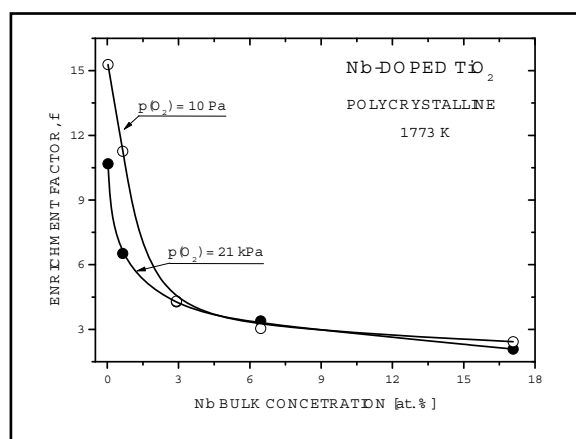


Fig. 3: Effect of oxygen activity on the enrichment factor for Nb segregation in Nb-doped TiO₂

It is clearly apparent from the results in Figures 3 and 4 that Nb segregation can be controlled to a large extent through control of oxygen activity, and also through selection of the bulk dopant concentration. Consequently, segregation promises to become a useful tool in the imposition of desired functional properties.

CONCLUSIONS

The effect of oxygen activity on the behaviour of Nb segregation in Nb-doped TiO₂ has been investigated. It has been observed that Nb surface segregation is favoured by low $p(\text{O}_2)$, especially for Nb bulk concentrations of less than 3 at % Nb. This effect has been related to the predominating defect disorder. Specifically, it has been speculated that segregation at high oxygen activity involves the migration of titanium vacancies, which would be expected to be much slower than the migration of electrons, expected at low oxygen activity. While it is not certain whether the present results represent equilibrium segregation (due to the absence of kinetic information), it is certain that the observed behaviour has a tendency towards equilibrium, which has formed the basis for the results interpretation. Finally, the observed results provide substantial evidence that segregation may be used as a tool for imposing specific functional properties in materials such as TiO₂.

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