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The effect of the valence state of titanium ions on the hydrophilicity of ceramics in the titanium–oxygen system

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Abstract

Ceramics from the titanium–oxygen system were prepared by sintering TiO_2 and Ti_2O_3 powders at 1400 °C in air or in Ar/H_2 (7%). The surface compositions of the TiO_2, the non-stoichiometric TiO_{2-x} and the Ti_2O_3 ceramics, studied with X-ray photoelectron spectroscopy, are discussed in terms of their chemical composition, with particular emphasis on the valence state of the titanium ions. The correlation between the valence state of the titanium ions at the surface and the water-contact angle was examined. The presence of Ti^{3+}, which can be introduced at the titanium–oxygen ceramic surface by sintering the ceramic in lower oxygen partial pressure, is related to a significant decrease in the water-contact angle. TiO_2 ceramics with just Ti^{4+} at the interface had a water-contact angle of 67°; however, the non-stoichiometric TiO_{2-x} and Ti_2O_3/Ti_3O_5 with Ti^{3+} at the interface had lower water-contact angles, i.e., 26° and 18°, respectively. The wettability of ceramics in the Ti–O system can be improved by introducing Ti^{3+} at the ceramic interface.

Keywords: Sintering; Defects; Surfaces; TiO_2; Sensors; Wetting

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1. Introduction

TiO_2 attracts particular interest because of two photo-induced phenomena, i.e., the photocatalytic and superhydrophilic effects.[1–4] TiO_2 has the ability to decompose many organic compounds due to the photocatalytic effect, a phenomenon that has been studied extensively.[5–7] When TiO_2 is illuminated with photons whose energy is equal to or greater than the TiO_2 band-gap energy, E_g, these photons are absorbed, and as a consequence electron–hole pairs are created. The electron–hole pairs further dissociate into free photoelectrons in the conduction band and photo-holes in the valence band. These photo-generated carriers can react with oxygen and water from the surroundings to produce the radicals $^{\bullet}O_2{}^{-}$ and $^{\bullet}OH^{-}$ that can recombine and decompose organic compounds.[4,6,7]

The second phenomenon, superhydrophilicity has been observed in TiO_2. When TiO_2 is illuminated with light of a specific wavelength, the surface becomes more hydrophilic, i.e., the water-contact angle decreases. Previous reports suggest that the super-hydrophilicity of TiO_2 after UV illumination is related to the reduction of Ti^{4+} to the Ti^{3+} state.[4,5] The electron that is formed under UV illumination tends to reduce the Ti^{4+} cations to the Ti^{3+} state and consequently oxygen vacancies are created. Water molecules can then occupy the oxygen vacancies, producing chemisorbed –OH groups, which increases the Van der Waals forces and the hydrogen-bonding interactions between the H_2O and the –OH, and as a result of this the hydrophilic properties are enhanced.[4,5] Fujishima et al.[4] reported that the water-contact angle of a TiO_2 anatase thin film is 15°, and that the angle decreases significantly after UV illumination. The water spreads over the anatase surface and the contact angle was estimated to be close to 0°. However, this increased hydrophilicity was not permanent and after a few hours in the dark the TiO_2 reverts to its more hydrophobic state.[4] For practical applications it is highly desirable that the surface of TiO_2 exhibits a high wettability with respect to water in addition to a photocatalytic effect. Such a surface ensures that surface contaminants are either photo-mineralised or washed away by water.

Titanium dioxide exists in three crystal structures,[8] i.e., rutile, brookite and anatase. When brookite and anatase are heated

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to temperatures between 700 and 920 °C they transform irreversibly to rutile.[9] Rutile crystallizes in a tetragonal structure with $a = 0.4594(3)$ nm and $c = 0.2959(3)$ nm.[10] Its properties are determined by the non-stoichiometry and the concentrations of various defects that can exist in the TiO_2 lattice. In addition, the properties of the TiO_2 surface can be greatly affected by the bulk structure and defects, as has been extensively reviewed.[11]

In addition to stoichiometric TiO_2, a lot of work has been done on non-stoichiometric TiO_{2-x}. The degree of non-stoichiometry significantly depends on the temperature and the oxygen partial pressure, as has been thoroughly reviewed.[12] Ti interstitials are regarded as the major defects at high temperatures.[13] The non-stoichiometry parameter x in TiO_{2-x} increases with increasing temperature and is reported to have an upper limit in air of 0.008 at 1000 °C and 0.016 at 1400 °C.[12]

For larger deviations from the TiO_2 stoichiometry, the oxide forms a series of compounds with ordered structures that appear between the non-stoichiometric TiO_{2-x} and Ti_2O_3. These structures are known as Magnéli phases,[14] and have the composition Ti_nO_{2n-1}, where $3 \leq n \leq 20$. Ti_2O_3 is isostructural with Al_2O_3, having the rhombohedral unit-cell dimensions $a = 0.54325(8)$ nm and $\alpha = 56.75(1)°$.[15] A phase diagram indicating all the compounds between Ti_2O_3 and TiO_2 is shown in Fig. 1.

There is a growing interest in understanding and possibly controlling the surface properties of TiO_2. Earlier investigations showed that the (1 1 0) surface possesses the lowest energy,[16] and for this reason it has been the most extensively studied. It was also confirmed that the hydrophilic-to-hydrophobic conversion of the TiO_2 surface can be induced by irradiating the sample with light of a specific wavelength.[17,18] However, the results concerning the contact angle of water on non-irradiated TiO_2 surfaces are rather inconsistent, with the angle ranging from 72°[18] to less than 10°.[19] There are numerous factors that can have an effect on the water-contact angle. For example, it is well known that atmospheric contaminants accumulate on a TiO_2 surface,[20] and as a consequence the contact angle increases. The surface roughness is also known to play an important role in influencing the water-contact angle.[17] Since the TiO_2 surface is hydrophilic, i.e., the reported contact angles are less than 90°, the lower contact angle may be the result of surface roughness. To the best of our knowledge even less information is available on the wettability of non-stoichiometric titanium oxide and Ti_nO_{2n-1} than for TiO_2.

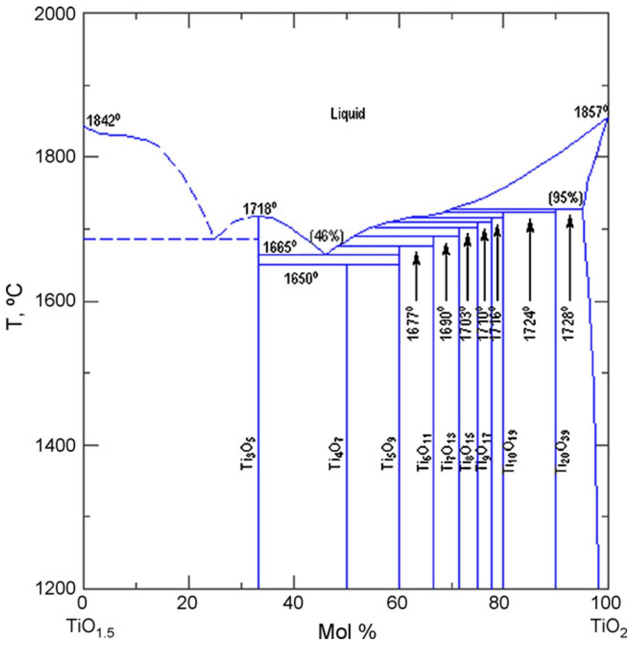

Fig. 1. Phase diagram of $TiO_{1.5}$–TiO_2.

The motivation for the present investigations was to find an alternative method, i.e., other than UV illumination, for enhancing the wettability of ceramics in the Ti–O system. Bulk TiO_2, non-stoichiometric TiO_{2-x} and Ti_2O_3 ceramics were prepared by sintering TiO_2 and Ti_2O_3 at various oxygen partial pressures, and the chemical compositions of their surfaces were investigated. The contact angle of water on the Ti–O ceramic surfaces is reported and correlated to the surface composition of the TiO_2, the non-stoichiometric TiO_{2-x} and the Ti_2O_3.

2. Experimental

For the experimental work we used commercially available TiO_2 (99.9%) and Ti_2O_3 (99.8%) powders, both from Alfa Aesar, Karlsruhe, Germany.

The non-stoichiometric TiO_2 powder (denoted TiO_{2-x}) was prepared from stoichiometric TiO_2 powder by heating it at 1400 °C for 2 h in Ar/H_2 (7%). After the heating, the powder had a dark colouration.

The Ti_2O_3 powder was high-energy milled in a planetary mill (Retsch, Model PM 400, Hann, Germany). A 250-ml tungsten carbide (WC) milling jar filled with 15 tungsten carbide balls of 20-mm diameter was used. A total of 200 g of powder was placed in the vial. The rotational speed of the supporting disk was set to 300 rpm. The milling conditions are detailed in reference.[21]

The TiO_2 ceramic was prepared from TiO_2 powder by sintering in air; the non-stoichiometric TiO_{2-x} ceramic was prepared from TiO_{2-x} powder by sintering in Ar/H_2 (7%); and the Ti_2O_3 ceramic was prepared from mechano-chemically activated Ti_2O_3 powder by sintering in Ar/H_2 (7%). All the powders were sintered at 1400 °C for 2 h.

During the thermal treatment of the TiO_{2-x} and Ti_2O_3 in Ar/H_2 (7%), titanium sponges were placed ahead of and behind the sample in the furnace to trap the impurities and ensure that only uncontaminated Ar/H_2 (7%) reached the sample. The furnace tube was used exclusively for thermally treating Ti–O ceramics and so any contamination from earlier firings is ruled out. The oxygen partial pressure in Ar/H_2 (7%) was measured using a Rapido 3100 Oxygen Analyser (Cambridge Sensotec Ltd., Cambridge, UK). The amount of oxygen in the gas before entering the tube furnace was 10^{-19} ppm at room temperature and at the exit of the tube furnace where the temperature was between 400 and 500 °C it was 10^{-17} ppm.

X-ray powder-diffraction data were collected from the samples at room temperature on an Endeavor Bruker AXS, Model D4 (Karlsruhe, Germany) diffractometer using Cu Kα radiation. The data were collected in the 2θ range from 20° to 70° in steps