Synchrotron Radiation Investigation of Thermal Stability and Grain-growth in Nanocrystalline TiO_2

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Introduction

The use of solar radiation to supply energy or to initiate chemical reactions is an active field of modern research. If a wide-band gap semiconductor like titanium dioxide (TiO_2) is irradiated with (UV) light, excited electron-hole pairs result that can be applied in solar cells to generate electricity or in chemical processes to degrade toxic compounds (organic and inorganic pollutants or biological materials such as viruses, bacteria, fungi, algae, and cancer cells). Therefore TiO_2 can be used for the purification of water and air, as well as for antibacterial purposes.

Titanium dioxide belongs to the family of transition metal oxides. In the beginning of the 20th century, industrial production started with titanium dioxide replacing toxic lead oxides as pigments for white paint. At present, the annual production of TiO_2 exceeds 4 million tons. It is used as a white pigment in paints (51% of total production), plastic (19%), and paper (17%), which represent the major end-use sectors of TiO_2. The consumption of TiO_2 as a pigment increased in the last few years in a number of minor end-use sectors such as textiles, food (it is approved in food-contact applications and as food coloring (E-171) under a EU legislation on the safety of the food additives), leather, pharmaceuticals (tablet coatings, toothpastes, and as a UV absorber in sunscreen cream with high sun protection factors and other cosmetic products), and various titanate pigments (mixed oxides such as $ZnTiO_3$ or $ZrTiO_4$).

Abstract

The ability to stabilize ultrafine-grained (UFG) microstructures within broad temperature and pressure ranges is nowadays essential to the use of the outstanding properties of nanomaterials in applications. An important step in the processing of fine powders is their consolidation into nanostructured bulk solids : there is a strong need to achieve control over the grain-growth process during this sintering stage. It was shown that porosity, excess free-volume, the presence of secondary phases or of solute elements, applied pressure and phase transitions influence the sintering (grain-growth and densification) behaviour of nanocrystalline materials. The crystallization, thermal stability and grain-growth of pure and Ag-doped nanostructured titania powders were here studied by *in-situ* high-temperature X-ray diffraction using synchrotron radiation.

References

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R. Nicula, **M. Stir**, C. Schick, E. Burkel, *High-temperature high-pressure crystallization and sintering behaviour of brookite-free nanostructured titanium dioxide: in situ experiments using synchrotron radiation*, Thermochimica Acta 2003, 403, 129-136.

R. Nicula, **M. Stir**, E. Burkel, *Synchrotron radiation investigation of thermal stability and grain-growth in pure and metal-doped nanocrystalline TiO_2*, Mater. Sci. Forum 2004, 467-470, 1307-1312.

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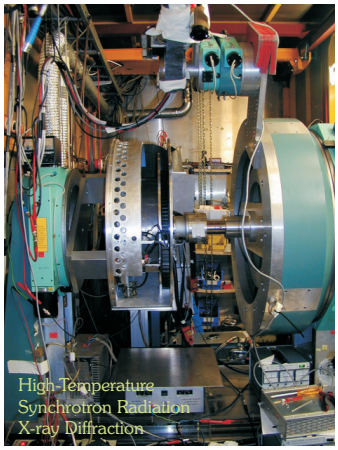
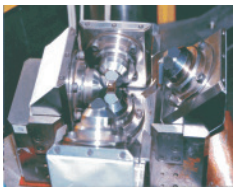
Sol-Gel Synthesis

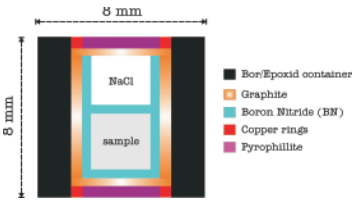
Tetraisopropyl orthotitanate (TTIP) and silver nitrate (Fluka) were used as main precursor materials. TTIP was first added to the solvent (ethanol, EtOH) under vigorous stirring. Distilled water was added dropwise to complete the hydrolysis reaction in an ultrasonic bath. The solution was further homogenized for several hours with a magnetic stirrer and aged at room temperature. This procedure yields nanostructured tetragonal phase anatase powders with brookite (20 wt.%, orthorhombic) as secondary phase. The addition of HCl during hydrolysis avoids the formation of brookite. Similar procedures were employed for the synthesis of metal-doped (Ag, Fe, Co) TiO_2 specimens. The as-prepared metal-doped specimens consist of nanocrystalline anatase : no traces of metal species or oxide phases are detected, pointing to a highly homogeneous dispersion of metal ions within the TiO_2 matrix.

Synchrotron Radiation Experiments



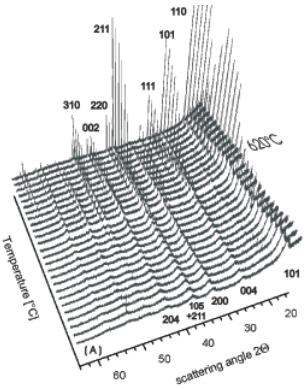
In-situ synchrotron radiation diffraction experiments were performed at the high-resolution B2 powder diffractometer and at the MAX80 instrument in HASYLAB (DESY Hamburg, Germany). Continuous heating and isothermal experiments were performed at various temperatures up to 1200°C and at pressures as high as 2.5 GPa. Image-plate or energy discriminating detectors were used which allow for the one-step acquisition of the diffraction patterns within a few minutes. The instrumental resolution functions were determined using standard NIST 660a LaB_6 specimens. The instrumental broadening correction was performed using the parabolic Halder-Wagner relation. An analysis of the diffraction line profiles using the double Voigt method indicated that strain broadening becomes negligible above 400°C. The corrected FWHM values were used to evaluate the grain size G according to the Scherrer equation.

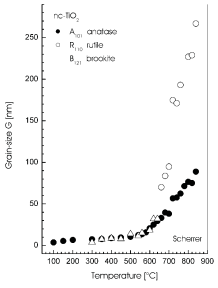


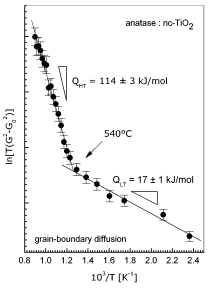


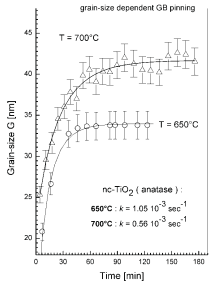
Results

Nanocrystalline Titanium Dioxide





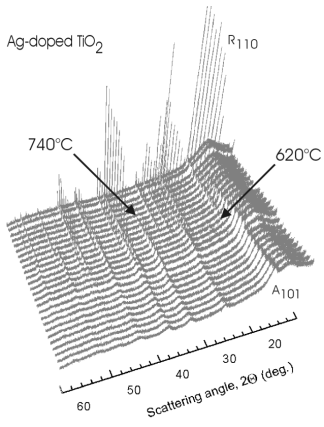




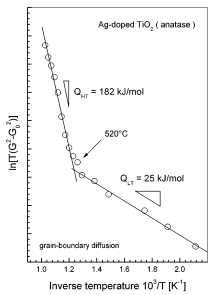
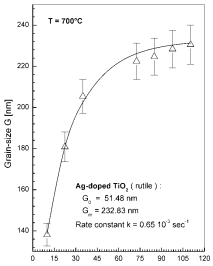
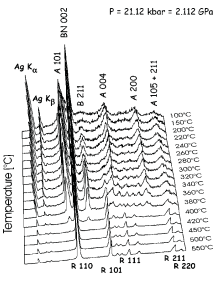
In-situ temperature- and time-resolved synchrotron radiation diffraction experiments were used to investigate the coarsening of nanocrystalline pure and metal-doped TiO_2 powder specimens. Normal grain growth (GB diffusion mechanism) is observed during constant rate heating (CRH) experiments :

$$G^2 - G_0^2 = k(T) \cdot t = 8\delta^2\gamma_0\mu_{GB}(T) \cdot t \qquad \mu_{GB}(T) = \frac{D_{GB}(T)}{RT} = \frac{D^0_{GB}}{RT}\exp\left(-\frac{Q_{GB}}{RT}\right)$$

Ag-doped TiO_2



Lock-up effects due to grain-size dependent grain boundary pinning were evidenced during isothermal annealing at high temperatures.

$$G_\infty^2 - G^2 = (G_\infty^2 - G_0^2) \cdot \exp(-k \cdot t) \qquad k = \frac{8\delta^2\gamma_0\mu_{GB}(T)}{G_\infty^2}$$

For the sol-gel-derived nanocrystalline titania powders valuable information was obtained on the activation energies for GB diffusion (CRH) as well as on the grain-growth rate values during isothermal annealing at high temperatures close to 700°C.