OATAO

Open Archive Toulouse Archive Ouverte

Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

Effect of H_2 on the Microstructure and Properties of TiO_2 Films Grown by Atmospheric Pressure MOCVD on Steel substrates

D. Duminica[a], F. Maury[a] and R. Hausbrand[b]

[a] CIRIMAT, CNRS/INPT/UPS, ENSIACET, 118 Route de Narbonne, 31077 Toulouse cedex 4, France.
[b] ArcelorMittal Research & Development Industry Gent, OCAS NV, John Kennedylaan 3, B-9060 Zelzate, Belgium.

TiO_2 thin films were deposited under atmospheric pressure by MOCVD in the range 400-600 °C on various steel substrates under hydrogen ambiance. It is unusual to study the growth of functional oxide layers under H_2 partial pressure, *i.e.* a reactive gas generally used as reductive atmosphere in CVD. Titanium tetra-isopropoxide was used as single source precursor of Ti and O. The growth rate of TiO_2 layers grown under nitrogen increases with the temperature and reaches a maximum in the range 500-550 °C. At these temperatures the diffusion of substrate ions enhances the formation of rutile leading to a lower UV photocatalytic activity. Addition of H_2 in the input gas phase during the deposition *(i)* reduces the formation of interface oxide layer, *(ii)* prevents the diffusion of cations from the steel substrate toward the TiO_2 layer and *(iii)* favors the growth of anatase. This leads to an increase of photocatalytic efficiency under UV irradiation.

1. Introduction

Over the last two decades there is a considerable interest for systems based on supported titanium oxide as photocatalyst for water and gas decontamination and photo-induced hydrophilic properties. A variety of supporting materials, such as glass, silicon, stainless steel webnet and quartz micro-fibres have been used. The selection of a substrate may influence the structure, homogeneity and adhesion of the TiO_2 film and consequently the efficiency of the photocatalyst. Among them, stainless steel is particularly attractive because of its low cost and wide use in many application fields such as architectural, food and pharmaceutical industry. Furthermore a TiO_2 film with a more negative cathodic photo-potential than the stainless steel can provide protection against corrosion (1). Additionally, electrically conducting supports offers the possibility of enhancing the photocatalytic activity of the TiO_2 overlayer by applying a positive bias on the catalyst with respect to a second electrode. The bias draws the photogenerated electrons away from the catalyst surface through the external circuit and limits their recombination rate with holes (2).

Atmospheric pressure metal organic chemical vapor deposition (AP-MOCVD) is a promising process for TiO_2 deposition because no vacuum system is required. It is known for its good capability for continuous deposition on a conveyor belt for large-scale production (3) and for the good control of the stoichiometry and microstructure of the films (4). The development of a continuous CVD process requires high deposition rates that is achieved using high flow rates of precursor (5).

Generally the photo-decomposition efficiency of organic pollutants by TiO_2 photocatalyst is influenced by the grain size and the TiO_2 structure. Because the photocatalytic reaction is a surface reaction, as the grain size becomes smaller, the specific surface area for reaction with organic pollutants increases (6). Therefore, the photo-decomposition efficiency of TiO_2 photocatalyst is higher when the grain size reaches the nanometric scale. Moreover, because the recombination rate of the electron-hole pairs in the rutile phase is faster than in anatase, it is well admitted that anatase is the most efficient phase for photocatalytic applications (7).

We reported previously the influence of the deposition temperature on the photocatalytic and hydrophilic properties of TiO_2 thin films deposited by AP-MOCVD on stainless steel (4, 8). It was shown that these properties decayed by increasing the deposition temperature in the range 400-600 °C and one of the reasons was the diffusion of cations from the substrate toward the growing film. These cations act as traps for the photo-induced electron-hole pairs and in addition they enhance the formation of rutile phase. Other authors pointed out the diffusion of Fe ions from stainless steel during high temperature treatment to form an underlayer of the rhombohedral phase Fe_2O_3 at the film-substrate interface (9). Cr and Ni still existed in the metallic state and only Fe was oxidized during TiO_2 film annealing owing to the highest sensitivity of iron toward oxygen (10). A degradation of hydrophilic properties of sol-gel TiO_2 deposited on stainless steel was reported after annealing between 350 and 500 °C for few hours due to cation diffusion (11).

Both to avoid oxidation of steel substrate and the detrimental effects of Fe ions diffusion on the photo-induced properties of the oxide layer, we have investigated the influence of H_2 in AP-MOCVD of TiO_2. It is unusual to study the growth of functional oxide layers under H_2 partial pressure, *i.e.* a reactive gas generally used to maintain a reductive atmosphere in CVD.

2- Experimental methods

A cold-wall vertical CVD quartz reactor, 5 cm in diameter, was used for the deposition of the layers. Stainless steel (AISI 304) and various low carbon steel plates were used as flat substrates. They were degreased with acetone and ethanol in ultrasonic bath and placed on a stainless steel sample holder (3.2 cm in diameter) heated by HF induction. The substrate temperature (350-650 °C) was measured using a thermocouple inserted in the sample holder. The gas streams were monitored using mass flow meters. The Titanium tetra-isopropoxide (TTIP) flow rates were maximized using a procedure described elsewhere (5).

The microstructure of the films was studied by X-ray diffraction (XRD) using grazing geometry (Cu Kα). The surface morphology was observed using a scanning electron microscope (SEM) and the film thicknesses were determined by reflectance spectroscopy and confirmed by observations of cross sections. SIMS depth profiles were carried out with a CAMECA IMS 4F6 instrument using a Cs^+ primary beam current of 50 nA over a 150 μm area.

The UV photocatalytic activity of the TiO$_2$ films was evaluated by measuring the decomposition rate of aqueous Orange G solutions (10 ppm) using UV-VIS spectroscopy according to a method described elsewhere (8).

3- Results and discussion

3.1 Growth of TiO$_2$ under nitrogen

The influence of deposition conditions under inert atmosphere (nitrogen) were recently reported in a companion paper (8) and additional results are commented hereafter.

Figure 1 shows the Arrhenius plot of the growth rate on Si(100) using a TTIP concentration of 0.9 % in the gas phase of pure nitrogen for short deposition time (1 min). The growth rate increases exponentially with the temperature leading to apparent activation energy of 102 kJ/mol. The maximum growth rate (as high as 1 μm.min^{-1}) is reached at approximately 550 °C. This behavior gives evidence for a kinetically controlled regime below 500 °C. For deposition temperatures higher than 500 °C homogeneous gas phase nucleation of TTIP was observed during the run with the formation of TiO$_2$ powder. In the high temperature range 500-550 °C the diffusion regime is very narrow and a depletion regime starts rapidly for temperatures higher than 600 °C as a result of the consumption of precursor by homogenous nucleation. The maximum deposition rate which is one of the most important parameters for the technological transfer of the process to a conveyor belt reactor is obtained for a deposition temperature around 550 °C. Under this condition no contamination of the films by powder particles was observed for short deposition time.
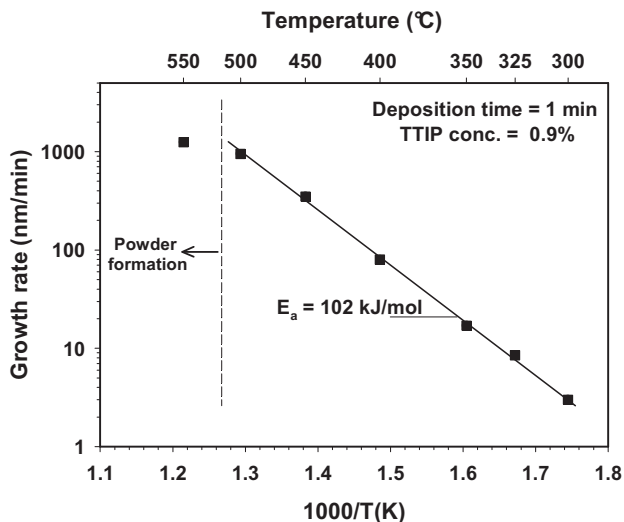

Fig. 1: Arrhenius plot of the growth rate of TiO$_2$ on Si(100) using TTIP concentration of 0.9 % in pure nitrogen atmosphere (total flow rate = 5500 sccm, deposition time = 1 min). The apparent activation energy Ea was 102 kJ/mol. Above 500-550 °C homogeneous gas phase nucleation of TTIP leads to powder formation.

Similar kinetic data were obtained on stainless steel substrates. However, at 550 °C the diffusion of ions from the substrate into the growing film is relatively high, which enhances the nucleation of rutile detrimental to anatase. According to experimental deposition diagrams reported in (8), the increase of the TTIP mole fraction is a solution to deposit anatase even at temperature higher than 550 °C. However, growth of nanometric thick TiO_2 films (thickness < 100 nm) on steel in the temperature range 500-550 °C requires a good control of the interface between the substrate and the growing film because an intermediate layer can be formed. Such a control is not easy using high TTIP mole fractions because it favors the growth of large TiO_2 crystals.

3.2. Anatase/rutile competition on stainless steel substrates

Very thin TiO_2 films (thickness < 200 nm) were grown on stainless steel using TTIP concentration of 0.01 % under nitrogen atmosphere in the temperature range 500-550 °C. The films are well crystallized, single phased and exhibit essentially the rutile structure. The formation of rutile at relatively low temperature (500 °C) on stainless steel and low carbon steel was previously reported (8). This is somewhat unexpected because the films deposited in the same runs on Si(100) and quartz substrates are solely constituted of anatase. The formation of rutile/anatase mixture depends on the initial surface of the substrate. In the case of stainless steel, TiO_2 grows directly on the passivation layer, *i.e.* on the Cr-rich Cr,Fe mixed oxide layer of the stainless steel substrate as shown by TEM micrograph (fig. 2). Its thickness is approximately 20 nm, which is too thin to be detected by XRD. The surface oxide of stainless steel is assumed to be $FeCr_2O_4$ (12). Figure 2 shows that rutile preferentially grows directly on the passivation layer. Possibly the nucleation of anatase also occurs at the surface of the steel substrate but with a lower nucleation rate and to a lower extend (no clear evidence was found by TEM due the roughness of the interface). Increasing the thickness of TiO_2 layers, the anatase which grows more rapidly than rutile gradually takes place on the top of rutile.
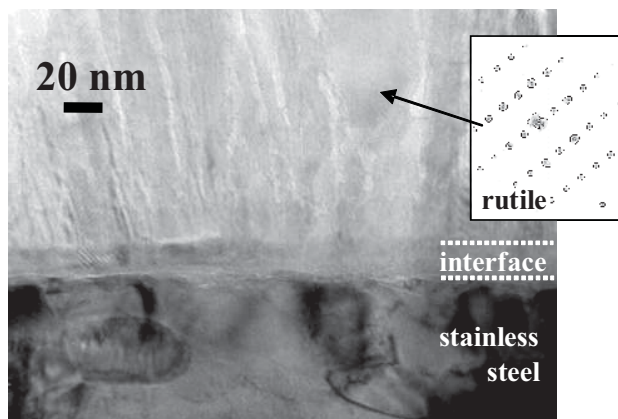

Fig. 2: TEM micrographs (cross section) of a TiO_2 layer (anatase/rutile mixture) grown on stainless steel at 550 °C using TTIP mole fraction of $1.8 \cdot 10^{-4}$ showing the TiO_2/substrate interface. The interface is a Cr-rich Cr,Fe mixed oxide. The rutile phase grows directly on this oxide (passivation layer).

3.3. Effect of H_2 on the morphology and the structure of TiO_2 layers

The addition of H_2 in the input gas phase changes slightly the surface morphology of TiO_2 without major change of the growth rate. Figure 3 shows that the average grain size decreases by increasing the H_2 partial pressure. The TiO_2 grain size decreases from about 250 nm without H_2 to less than 100 nm using 10 % H_2.
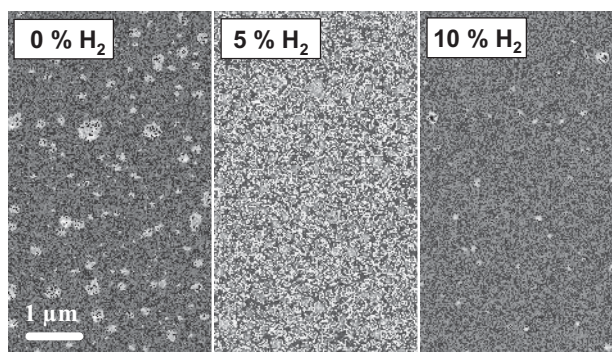

Fig. 3: SEM surface micrographs of TiO_2 layers grown on stainless steel substrates at 550 °C using different amount of H_2 in the input gas phase and a TTIP mole fraction of 10^{-4}.

Interestingly, the addition of a slight amount of H_2 (5-10 %) in the reactive gas phase changes the structure of TiO_2 layers. The growth of anatase is favored to the detriment of rutile even for very thin layers as shown in figure 4. Indeed, at 550 °C, using TTIP mole fraction of 10^{-4} under nitrogen atmosphere, rutile is principally deposited for films with a thickness ~200 nm, while using 10 % H_2 in the input gas phase an anatase/rutile mixture is formed with anatase as dominant phase. Even for larger amount of H_2 (15 %) the deposited layer exhibits an anatase-rich mixed structure without any evidence for substoichiometric oxides (*e.g.*, Ti_3O_5, Ti_2O_3...), which could result from the reduction of the Ti(IV) of TTIP. This means that under these conditions, the reduction of the TiO_2 film does not occur during MOCVD growth.

Figure 5 shows SIMS concentration profiles of two TiO_2 thin films (150 nm thick) grown on low carbon steel substrates at 550 °C without and with 10 % H_2 in the input gas phase. The Ti profiles show the presence of two regions: the first corresponding to the TiO_2 film and the second corresponding to the diffusion of Ti into the steel substrate. The Fe profile reveals also the presence of iron in the deposited film. The iron signal in TiO_2 grown without H_2 is relatively high and constant through the thickness of the deposited film revealing a significant diffusion. By contrast, the relative concentration of iron in the TiO_2 film is significantly reduced when H_2 is added in the input gas phase. The intensity of the Fe signal near the external TiO_2 surface is lower by almost two orders of magnitude when the film is grown under H_2 partial pressure. This lower iron concentration in the growing film increases the proportion of anatase.
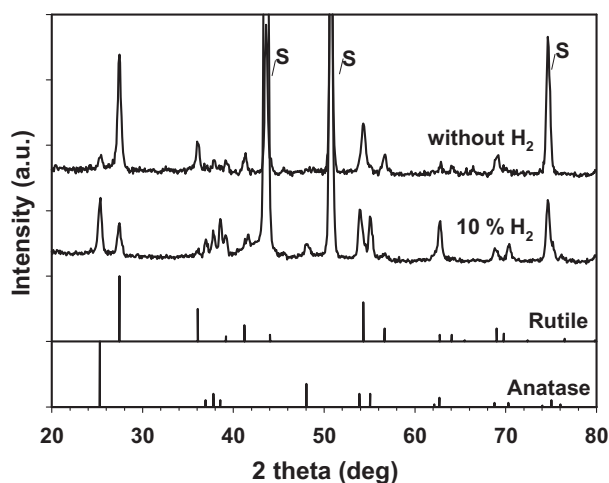
Fig. 4: XRD grazing patterns (incidence angle 2 deg) of TiO_2 layers grown at 550 °C on stainless steel using TTIP mole fraction of 10^{-4} without (top) and with 10 % H_2 in the input gas phase (film thickness ~ 200 nm). The peaks labelled S originate from the substrate.

The reduction of the average grain size observed for films grown under H_2 ambient coupled with an increase of the anatase/rutile ratio and lower cation diffusion in the TiO_2 film are three requirements beneficial to the photocatalytic properties.
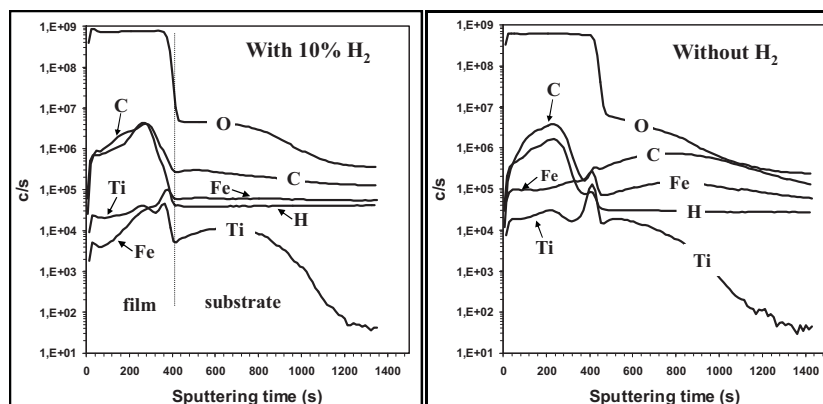

Fig. 5: SIMS concentration profiles of TiO_2 films (~150 nm) grown on low carbon steel substrates at 550 °C using TTIP mole fraction of 0.01 % without (right) and with 10 % H_2 (left) in the input gas phase.

3.4. Effect of H_2 on the photocatalytic activity of TiO_2 layers

Figure 6 shows the relative variation of the concentration of Orange G aqueous solutions under UV irradiation decomposed by TiO_2 layers (~ 300 nm thick) grown on stainless steel at 550 °C without and with 10 % H_2. A significant increase of the

photocatalytic activity is obtained when TiO_2 films are grown under H_2 atmosphere. The degradation rate (K) is improved by 44 %. As excepted we attribute this behaviour to *(i)* the smaller TiO_2 average grain size (fig. 3), *(ii)* the increase of the anatase proportion in the films (fig. 4) and likely *(iii)* a lower contamination of by cations originating from the steel substrate (fig. 5).
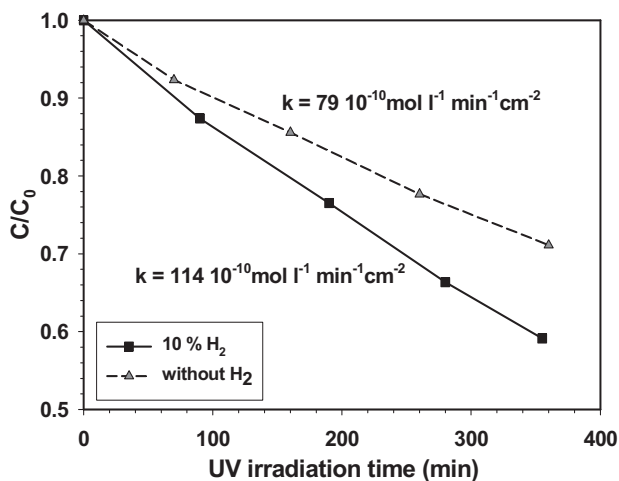

Fig. 6: Relative variation of the concentration of Orange G aqueous solutions (10 ppm) photocatalytically decomposed under UV irradiation by TiO_2 thin layers (~300 nm thick) grown on stainless steel at 550 °C without and with 10 % H_2.

Various authors have reported a beneficial influence of H_2 on the photocatalytic activity of TiO_2 powders due to a possible increase of the holes lifetime reducing the recombination centers in the bulk. For instance, enhanced photocatalytic activity of TiO_2 powder was found by thermal reduction treatment of the powder under hydrogen at 550 °C (13). The authors proposed that the reduction of TiO_2 particles raised their Fermi level and increased the height of the barrier that repelled electrons from the surface of the particles because more Ti^{3+} was present at this location. Besides Ti^{3+} species, the presence and effect of oxygen vacancies was reported in the H_2-reduced TiO_2 powder. In addition, they also demonstrated the presence of hydroxyl groups in the treated TiO_2, but it is not clear whether the improvement in the photoactivity of the TiO_2 catalysts after H_2 reduction treatment resulted from all the species, *i.e.* O-vacancies, Ti^{3+} and OH groups, or only from some of them (14).

Liu *et al.* showed a significant enhancement by using the H_2-treated TiO_2 photocatalysts and the optimum temperature for the H_2 treatment was found in the range 500–600 °C (15). In situ electron paramagnetic resonance signal intensity of O-vacancies and Ti^{3+} associated with the photocatalytic activity proved the presence of these species in the lattice of the H_2-treated TiO_2 and revealed that both contributed to the improvement of photocatalytic activity.

In all these works, TiO_2 powders were used. In the present contribution we demonstrated the beneficial effect of H_2 in a one step preparation of a photocatalyst that is supported on steel substrate to produce active functional surfaces.

4. Conclusions

TiO_2 thin films were deposited under atmospheric pressure by MOCVD in the temperature range 400-600 °C on stainless steel and low carbon steel substrates under H_2 partial pressure. TTIP was used as Ti and O single source precursor. The growth rate of TiO_2 layer is thermally activated and reaches a maximum (1 $\mu m.min^{-1}$) in the range 500-550 °C either under pure N_2 or H_2/N_2 atmosphere. At this relatively high temperature the diffusion of cations from the substrate induces the formation of rutile. Addition of H_2 in the reactive gas phase during the deposition likely reduces the oxide at the surface of the steel in the early stage of the growth and prevents the diffusion of cations as Fe^{3+} and Cr^{3+} in the growing layer. As a result the proportion of rutile is significantly decreased in favor of anatase and the average TiO_2 grain size is decreased from about 250 to 100 nm. A significant improvement of the photocatalytic activity under UV irradiation is observed for films grown using 10 % H_2 (increasing the degradation rate by more than 40 %). Therefore efficient supported photocatalysts were deposited on steel by a one step atmospheric pressure MOCVD process without oxidizing the substrate.

References

1. Y. Ohko, S. Saitoh, T. Tatsuma and A. Fujishima, *J. Electrochem. Soc.*, **148**, B24 (2001)
2. K. Vinodgopal, S. Hotchandani and P.V. Kamat, *J. Phys. Chem.*, **97**, 9040 (1993)
3. G.A. Battiston, R. Gerbasi, M. Porchia and L. Rizzo, *Chem. Vap. Deposition*, **5**, 73 (1999)
4. F.-D. Duminica, F. Maury and F. Senocq, *Surf. Coat. Technol.*, **188-189**, 255 (2004)
5. F. Maury, F.-D. Duminica and F. Senocq, *Chem. Vap. Deposition*, **13**, 638 (2007)
6. Q. Zhang, L. Gao and J. Guo, *Appl. Catal. B: Environ.*, **26**, 207 (2000)
7. J.-M. Herrmann, *J. Catal. Today*, **53**, 115 (1999)
8. F.-D. Duminica, F. Maury and R. Hausbrand, *Surf. Coatings Technol.*, **201**, 9304 (2007)
9. A.H.C. Chan, J.F. Porter, J.P. Barford and C.K. Chan, *J. Mater. Res.*, **17**, 1758 (2002)
10. Y. Zhu, L. Zhang, L. Wang, Y. Fu and L. Cao, *J. Mater. Chem.*, **11**, 1864 (2001)
11. S. Permpoon, M. Fallet, G. Berthomé, B. Baroux, J.C. Joud and M. Langlet, *J. Sol-Gel Sci. Tech.*, **35**, 127 (2005)
12. M. Da Cunha Belo, M. Walls, N.E. Hakiki, J. Corset, E. Picquenard, G. Sagon and D. Noel, *Corrosion Science*, **40**, 447 (1998)
13. A. Heller, Y. Degani, D.W. Johnson and P.K. Gallagher, *J. Phys. Chem.*, **91**, 5987 (1987)
14. L.A. Harris and R. Schumacher, *J. Electrochem. Soc.*, **127**, 1186 (1980)
15. H. Liu, H.T. Ma, X.Z. Li, W.Z. Li, M. Wu and X.H. Bao, *Chemosphere*, **50**, 39 (2003).