

Reduction of TiO_2 assisted by a microwave plasma at atmospheric pressure

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Abstract

The reduction of rutile- TiO_2 thin foils by microwave plasma created in a resonant cavity at atmospheric pressure gives a $\text{TiO}/\text{Ti}_2\text{O}_3/\text{Ti}_3\text{O}_5$ sequence at 973 K for a 5% H_2 –He mixture. The efficiency of the reduction process is strongly affected by a slight change of the gas composition. The intensity of the H_α transition measured by optical emission spectroscopy was used to determine experimental conditions where the temperature of the substrate could be adjusted between 980 and 1090 K without changing the hydrogen concentration close to the surface substrate. In these conditions, no titanium layer could be detected by grazing angle X-ray diffraction. A $\text{TiO}/\text{Ti}_2\text{O}_3$ sequence is observed with an anatase–rutile transition that occurs above a treatment temperature of 1020 K. The overall reduction rate is close to $1 \mu\text{m h}^{-1}$ under the chosen conditions. The evolution of the thickness of the Ti_2O_3 layer below 1060 K demonstrates that the deoxidation mechanism is not simply related to the atomic hydrogen concentration in the gas phase.

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1. Introduction

With the forthcoming increase of the European environmental constraints, an urgent need has appeared to develop alternative processes to aqueous surface treatments of metallic alloys. The cold plasmas are promising ways to provide friendly environmental technologies [1,2]. On the other hand, plasma sources operating at atmospheric pressure are low cost technologies and their upscaling is often direct for flat substrates [3]. Consequently, many studies with atmospheric plasmas have been developed during the last decade. Among the possible applications, the reduction of metallic oxides by plasma is often needed to prepare the surface of the substrates before treatment [4] or to deoxidise materials which contain metals [1,2]. Many works have been performed using low pressure plasma containing hydrogen with either direct current [5], radio-

frequency [6] or microwave sources [7,8]. Low energy ion bombardment can improve the reduction of surface oxides in some cases [5], but it is to ban for the treatment of materials like GaAs [9] or InP [4].

Most atmospheric pressure plasmas used for surface treatments are Dielectric Barrier Discharges, Atmospheric Pressure Glow Discharge or torches [10]. Functionalisation of polymers [11], surface cleaning [12] or chemical vapour deposition [13] are possible applications of these sources. The plasma used for this work is a resonant cavity. This technique helps us to create a highly ionised plasma (compared with APGD) without walls. It is useful to avoid the etching of any other surface than the substrate and the subsequent contamination of the gas phase by the etching by-products [14]. Atmospheric pressure deoxidation of CuO has recently been investigated [15] at lower temperature than in the present work. Indeed, according to Ref. [7], the reduction kinetics, and thus the treatment temperature, would depend on the metal–oxide binding energy. The purpose of the present work is thus to define experimental conditions in which the reduction of rutile which has a

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strong oxygen–metal binding energy (672 kJ/mol [16]) is possible at atmospheric pressure.

2. Experimental details

Fig. 1 shows a schematic of the experimental set-up. The reactor is made of a 30 mm outer diameter quartz tube passing through a 2.45 GHz microwave resonant cavity. The resonant cavity has been calculated and designed to create a wall-less plasma and to avoid any change in the plasma composition by chemical etching at the boundaries. The microwave power delivered to the plasma (i.e. the difference between the incident and the reflected powers), the gas composition, i.e. the amount of hydrogen in helium, and the location of the sample in the discharge (hereafter referred as the z coordinate defined in Fig. 1) determine the temperature of the substrate (Fig. 2) and the density of active species. Optical emission spectroscopy is performed by means of an optical fibre connected to a Jobin-Yvon HR640 spectrometer with a R928 Hamamatsu photomultiplier tube and a Spectralink control and data acquisition system.

In this work, the flow rate of helium is fixed at 2000 sccm ($1 \text{ sccm} = 1.66 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$) and the microwave power delivered to the plasma is 285 W. The treatment time is 4 h. One major advantage of this set-up is the simplicity of its arrangement, whereas the temperature and the position of the sample cannot be decoupled. The temperature is measured by a thermocouple inserted in the back of the substrate holder and by an infrared pyrometer located on the top of the quartz tube. Both measurements give similar results (with an accuracy of 5%) when the substrate does not enter too far in the discharge ($z < 10 \text{ mm}$). Otherwise, the thermocouple acts as an antenna and only the temperature indicated by the infrared pyrometer is correct.

The substrates ($5 \times 5 \text{ mm}^2$) are synthesized by oxidation in the air at 1173 K of pure titanium foils (purity: 99.6%) of 25 μm in thickness for a sufficiently long time to obtain a complete conversion to an oxide. Titanium oxidation produces a complete transformation of the metal into dense

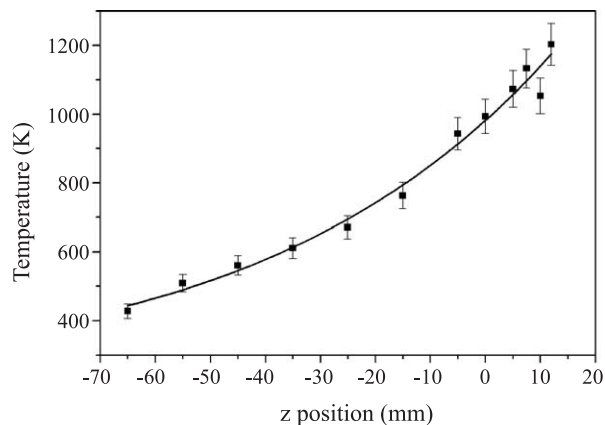


Fig. 2. Evolution of the substrate temperature as a function of its position in an He–5 vol.%H₂ plasma. The microwave power delivered to the plasma is 285 W.

TiO₂ (rutile) as verified by X-ray diffraction. The titanium oxide grows by inward diffusion of oxygen to the metal–oxide interface [17]. The reduction treatment by an atmospheric pressure plasma is applied to the rutile foil and results are analysed by optical micrographs and grazing angle X-ray diffraction.

3. Results and discussion

In a first step, the reduction of TiO₂ is studied as a function of the gas composition at $973 \pm 25 \text{ K}$. The position of the sample is thus adjusted at each experiment to set the temperature at a constant value. The hydrogen content in helium is varied from 1 to 10 vol.%. All the experiments of this set have been done twice and the 5 vol.% H₂ experiment has been done three times to be sure of the reproducibility. To clearly identify the reduced layers and their respective position with respect to the topmost surface, GAXRD analyses were performed on each reduced substrate. Results using a fixed grazing angle of 2° are provided in Fig. 3. The identification of the different phases is reported in Table 1.

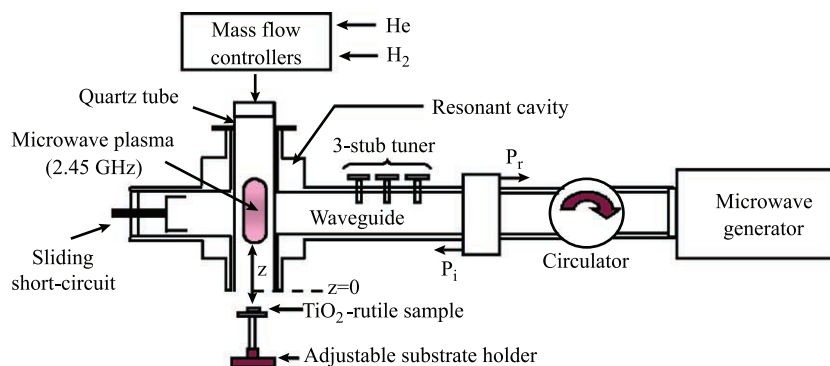


Fig. 1. The experimental set-up based using a microwave resonant cavity plasma. TiO₂ rutile thin foils are synthesized by oxidation in the air at 1173 K of 25 μm thick titanium foils. For the reduction step under plasma at atmospheric pressure, the flow rate of helium is fixed equal to 2000 sccm and the microwave power delivered to the plasma is 285 W. The treatment time is 4 h.

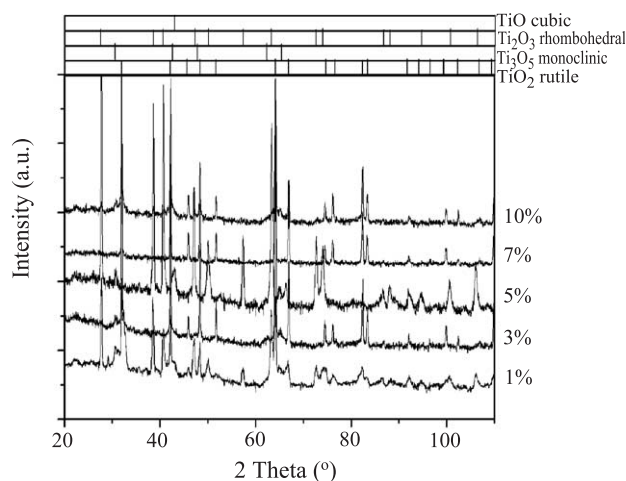


Fig. 3. Grazing angle X-ray diffraction patterns of the reduced substrates under different hydrogen content in helium. The temperature is 973 K. A fixed grazing angle of 2° is used. Only useful peaks for phase identification are reported in the cartridge.

Reduction of rutile is clearly observed except at 7% of hydrogen. The presence of Ti_3O_5 at 10% with a weak intensity let us think that the reduction above 5% of H_2 occurs but with a very low kinetics. Below 5%, the presence of Ti_3O_5 and Ti_2O_3 shows that the reduction of rutile is also possible and occurs with a higher rate than above 5%.

The highest rate is obviously measured at 5% since TiO is detected. The presence of this phase has been evidenced from X-ray diffraction patterns made under different grazing angles. This analysis is reported in Fig. 4. The TiO peaks increase as the angle decreases, showing that TiO is the topmost layer. Ti_3O_5 and Ti_2O_3 are also detected, showing a sequence of oxides which satisfies the Ti–O binary phase diagram [18]. Despite the TiO layer is very thin, its presence demonstrates that the reactivity of the plasma is strongly dependent on the gas phase composition in a very narrow range. Moreover, no titanium grows at the topmost surface. The gas phase reduction potential is probably not high enough to reach the metallic state. The reason for this is not clear yet. Further experiments are required to analyse the gas phase during the reduction step. To try to understand how the reduction occurs, a second set of experiments has been carried out.

Table 1
Titanium oxides detected by X-ray diffraction at different contents of hydrogen in helium

		Hydrogen content in helium (vol.%)				
		1%	3%	5%	7%	10%
Titanium oxides	TiO_2 -rutile	w	s	nd	s	s
	Ti_3O_5	w	w	s	nd	w
	Ti_2O_3	s	nd	s	nd	nd
	TiO	nd	nd	weak	nd	nd

The intensity of the strongest peak of each phase is qualitatively reported as weak or strong if detected. The position of the sample is unchanged. w=weak; s=strong; nd=not detected.

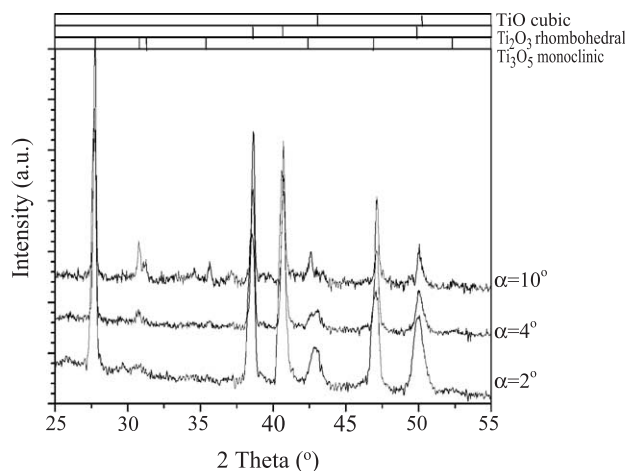


Fig. 4. X-ray diffraction patterns at different grazing angles of the reduced substrate at 5 vol.% of hydrogen in helium. The temperature is 973 K. Only useful peaks for phase identification are reported in the cartridge.

The influence of the temperature is investigated. The previous results have shown that the composition of the gas phase is a parameter that must be controlled accurately. The approach chosen here assumes that the Balmer transition of atomic hydrogen (H_α : $n=3 \rightarrow n=2$ at 6563 \AA) could be an indicator of the concentration of the active species (atomic hydrogen) responsible for the reduction process. Indeed, in a helium–hydrogen plasma, the optical emission of the radiative hydrogen atoms is easily observed with a spectrometer. The measurement of this transition is thus performed for different position of the substrate in the plasma (Fig. 5) and different concentrations of hydrogen in the carrier gas. The emitted light is collected through a 2 mm diameter collimator located in front of regularly spaced holes made in the resonant cavity. An arbitrary intensity of this transition was then chosen to determine different

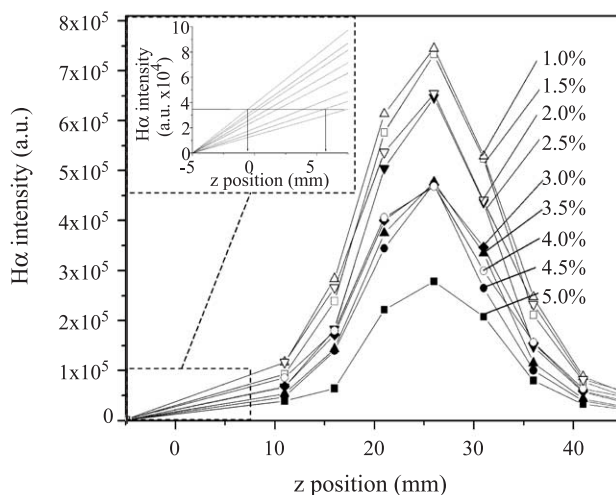


Fig. 5. Intensity of the H_α transition at 6563 \AA measured by optical emission spectroscopy as a function of the gas phase composition and the position of the substrate. The experimental conditions retained for the second set of experiments are magnified.

Table 2

Titanium oxides detected by X-ray diffraction at different contents of hydrogen in helium

		Hydrogen content in helium (vol.%)						
		1.0%	1.5%	2.0%	2.5%	3.0%	3.5%	4.0%
Temperature (K)		980	990	1000	1010	1020	1060	1090
Titanium oxides	TiO ₂ -rutile	nd	w	w	s	s	nd	nd
	TiO ₂ -anatase	nd	nd	nd	nd	nd	w	s
	Ti ₂ O ₃	s	s	s	s	w	s	s
	TiO	nd	nd	nd	nd	nd	s	s

The intensity of the strongest peak of each phase is qualitatively reported as weak or strong if detected. The position of the sample is changed to keep the H_{α} transition constant.

w=weak; s=strong; nd=not detected.

positions having the same intensity of the H_{α} transition and thus, the same concentration of hydrogen atoms. The corresponding temperatures are reported in Table 2.

GAXRD results of the reduction treatments at these positions are presented in Fig. 6. The grazing angle is fixed at 4° . The identification of the different phases is reported in Table 2. First, the presence of anatase above 1020 K reveals a transformation of the rutile phase, probably during the cooling of the sample which is done under a He–H₂ flow as soon as the plasma is turned off. This temperature is within the range of reported values by numerous works where the anatase–rutile transition has been determined [19–21]. Next, the reduction rate increases as the temperature increases. A thick TiO phase is obtained above 1020 K but, as in the first set of experiments, no titanium is detected. Below 1020 K, Ti₂O₃ is synthesised, showing that the reduction of rutile is efficient. Contrary to the first set of experiments, the Ti₃O₅ layer is not detected, whereas it is very likely present from a thermodynamic point of view. Then, it can be assumed that its thickness is probably too weak to be detected.

To estimate the reduction kinetics, cross section micrographs of the reduced substrate have been done. At 3.5 vol.% H₂, it is depicted in Fig. 7. At least, two different

layers are easily observed. They correspond to the phases detected using X-ray diffraction. We can estimate the thicknesses of TiO and Ti₂O₃ after a 4-h treatment (for 3.5% of H₂) to 4 ± 0.2 and 5 ± 0.2 μm . The overall reduction kinetics is then close to 2 $\mu\text{m/h}$ at 1060 K. Below 1060 K, only the Ti₂O₃ layer can be observed.

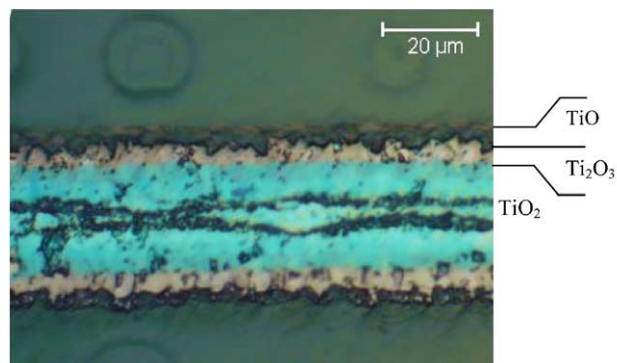


Fig. 7. Optical micrograph of the cross section of a substrate reduced at 1060 K by a 3.5% H₂–He plasma at atmospheric pressure. The Ti₃O₅ layer (which should be located between Ti₂O₃ and TiO₂) is probably too thin to be distinguished by the technique.

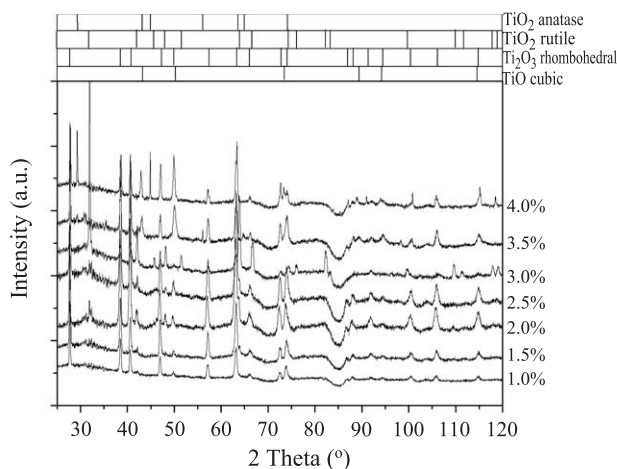


Fig. 6. Grazing angle X-ray diffraction patterns of the reduced substrates under different hydrogen contents in helium. The temperature is 973 K. A fixed grazing angle of 4° is used. Only useful peaks for phase identification are reported in the cartridge.

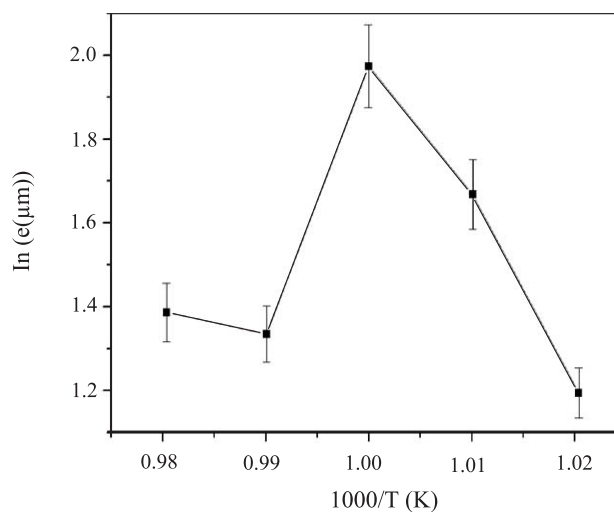


Fig. 8. Arrhenius plot showing the evolution of the Ti₂O₃ thickness as a function of the temperature between 980 and 1020 K.

The deoxidation mechanism is obviously activated by the temperature. However, if one assumes that the concentration of the active species responsible for the removal of oxygen from the surface oxide is constant, the core of the material being TiO_2 , the potential gradient of oxygen must be constant. The effect of the temperature on a diffusion limiting reduction step should then follow an Arrhenius behaviour. The evolution of the thickness of the Ti_2O_3 layer is plotted in Fig. 8 as a function of the reciprocal of the temperature below 1060 K at which the TiO phase appears. A complex dependence is observed. When the temperature rises, the thickness of the layer increases first and then suddenly decreases. An Arrhenius law is probably followed at low temperature. At 1010 and 1020 K, the decrease of the thickness of the Ti_2O_3 layer is not explained yet. The reduction mechanism is probably not simply related to the concentration of atomic hydrogen in the gas phase as determined by optical emission spectroscopy. It may be due to the method used to determine this density since atmospheric plasmas are not optically thin media. In this case, the emission of the H_α transition is only meaningful for the most outer parts of the plasma and it is probably not a good way to estimate H atom density [22]. Further investigations are then required to clarify the mechanism of reduction of TiO_2 .

4. Conclusion

Several conclusions can be drawn from the work presented in this paper. First, the reduction of TiO_2 is possible at 973 K and the configuration of the reduced layers may evolve depending on the concentration of hydrogen in helium within a short range of composition. Secondly, titanium is never detected as a result of the reduction process. Third, the mechanism responsible for the reduction of the TiO_2 substrate is not simply correlated with the concentration of atomic hydrogen in the gas phase. Further analyses are thus required to improve this process and provide a better understanding of the general phenomena that govern the reduction process.

Acknowledgements

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