Synthesis of Titanium via Magnesiothermic Reduction of TiO_2 (Pigment)

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Abstract

During the last decade a variety of investigations have been conducted to find alternative routes to the Kroll process for production of titanium metal. The reduction of titanium dioxide by magnesium is one of these approaches and currently under experimental research at RWTH Aachen University, funded by DAAD. The process will lead to titanium qualities of less than 2% oxygen content and such the magnesiothermic reduction can only represent an intermediate step in the entire reduction-deoxidation process. Bearing in mind the local temperature of the reaction, a good control of the highly exothermic behaviour, the partial pressure of the magnesium gas in a closed reaction chamber will ensure an efficient way for recovering of titanium metal. Subsequent leaching allows to deliver the titanium to a deoxidation process. By-products from this reaction can be recycled in order to improve the economic feasibility of this approach. The paper will present thermochemical modelling of the process as well as the results of bench-scale experiments leading to a draft of a titanium powder process chain.

1 Introduction and target

Since the 1950's, titanium producers have been looking for easier and cheaper processes to replace the Kroll process. Between them well-known investigated processes are PPR (Preform reduction process) [1], FFC (Fray-Farthing-Chen) [2] and OS (Ono-Susuky) [3]. These processes use titanium dioxide, calcium and calcium chloride as charge materials to produce titanium either by electrochemical reactions with dissolved calcium or by metallothermic reduction with calcium vapour. Although the obtained titanium has very low oxygen content, such processes are up to now hardly scalable and no pilot plants have been developed so far. Over the last 10 years IME is engaged in the development of alternative processes to produce titanium alloys or to recycle titanium scrap, such as the aluminothermic reduction from titanium dioxide [4], deoxidation by active slag [5], and recycling of titanium scrap by vacuum induction melting VIM [6]. Nowadays, there is an ongoing research on titanium extraction by magnesiothermic reduction in order to produce powder titanium targeting on less than 2% oxygen approximately as the first step in the process chain of titanium powder production from titanium dioxide. Currently titanium powder is produced by melting of titanium ingots, milling of brittle hydride titanium or from by-products of the sodium sponge making process. Wrought metallurgy requires a multitude of processes and eventually ends with material buy-to-fly ratios of less than 17%. In contrast, titanium powder metallurgy allows a greater material utilization of 70-95% (depending on the application) by making net near-shapes directly from powder [7]. A process to obtain titanium powder directly from titanium dioxide in few steps could become economically striking even more if the annual consumption of commercially pure (CP) titanium increases about 220%, as predicted by Norgate, if the cost decreases by 50% [8].

2 Magnesiothermic reduction

2.1 Equilibrium calculations

Less ignoble metals than titanium can be used to reduce titanium dioxide by metallothermic reduction. Those metals are e.g Mg, Al, Ca, Li and Zr. Among them, Mg and Al are especially attractive, due to their affordable price and low melting or boiling point. Aluminothermy can not produce pure metallic titanium with low oxygen contents at the same time because oxygen activity in the equilibrium slag is relatively high and overstochiometric aluminium charge causes formation of stable intermetallic alloys with titanium making it an attractive process to obtain alloys TiAlX [4]. Magnesium on the other hand can reduce titanium dioxide to metallic titanium for further treatment as charge material in common titanium processes. The magnesiothermic reduction can be represented by the following theoretical equation

$$TiO_2 + 2\,Mg = Ti + 2\,MgO \qquad (1)$$

This exothermic reaction has an enthalpy of -129.1 KJ/mol, an adiabatic process temperature of 1814°C and a Dautzenberg parameter of 2009 J/g . Dautzenberg parameters higher than 3000 J/g indicate that the reaction should be self propagating [10]. The adiabatic process temperature is calculated where the difference between the enthalpy of products in equilibrium at process temperature and the enthalpy of reactants in equilibrium at start temperature is zero [9]. This temperature value depends on the amount of reactive agents. Increasing the molar composition ratio φ reduces the process temperature, because the generated energy must be employed to heat or/and transform the magnesium excess to the equilibrium phase. The molar composition ratio can be described using the following equation:

$$\varphi = \frac{\eta Mg}{\eta TiO_2} \qquad (2)$$

Figure 1 shows the decrease of adiabatic temperature versus the increasing molar composition ratio φ calculated by FactSage®5.5 using the FACT53, SGSL and FToxide database. The reactants were chosen as follows: TiO_2 Rutile phase (FToxide), Mg solid phase (FACT53) and the products Ti were: Ti liquid phase and solid phase bcc_a2 (SGSL), Mg gas phase (FACT53), Mg liquid phase (FACT53) and MgO solid periclase (FToxide). The calculation was performed in 3 different step, the first one from 25°C up to the boiling point of magnesium (1094°C), the second one from the boiling point of magnesium up to the melting point of titanium (1668°C), and the third one at temperature higher than melting point of titanium to the maximal temperature process (1814°C). A molar composition ratio $\varphi \leq 2.7$ generate enough energy to evaporate all magnesium available in the reaction mix.

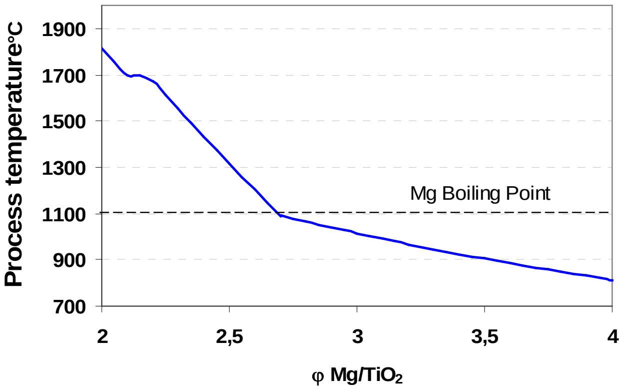

Figure 1: Adiabatic Process Temperature versus the increasing molar composition ratio φ

Titanium can reach valence numbers up to 4^+, allowing for many oxidation stages. At high oxidation states it forms titanium dioxide TiO_2 and the well-known Magnèli Phases, the oxides between $Ti_{10}O_{19}$ and Ti_4O_7. Their chemical formula can be calculated with the following model. Other oxides between Ti_3O_5 and TiO are called "high titanium oxides".

$$Ti_nO_{2n-1} \quad 4 \leq n \leq 10 \tag{3}$$

Magnesium has a low solubility in titanium, approximately 0.1% by weight at 1000°C [11]. For practical proposes this value can be considered as negligible. Magnesium and titanium oxide can form different titanates, such as $MgTiO_3$, Mg_2TiO_4 and Mg_2TiO_5. The ternary system of Ti-Mg-O was calculated with FactSage®5.5 using the FACT53 and SGTE database and shows different phases in thermochemical equilibrium at 1000°C. In Figure 2 the connection line between Mg and TiO_2 was traced to show possible equilibrium phases existing with variation of the molar composition ratio φ at 1000°C. 5 areas are presented by the points I to IV. A low magnesium ratio ($\varphi < 0.3$) forms Magnèli phases and magnesium titanates ($MgTiO_3$ or Mg_2TiO_5). Between point I and II ($0.3<\varphi <0.5$) the reaction forms Ti_2O_3 and magnesium titanates (Mg_2TiO_4 or $MgTiO_3$). Exceeding point II ($\varphi <0.5$) no formation of magnesium titanates happens and MgO is formed instead. Metallic titanium is obtained for the first time in the area between point III and IV ($1<\varphi <2$) in a mixture of

TiO and MgO. Finally phases of metallic titanium, magnesium oxide and the excess of magnesium are formed (φ < 2). Similar analyses can be made from 650 to 1300°C because the ternary diagrams present the same form, with the difference that at temperatures higher than 1090°C magnesium appears in gaseous form.

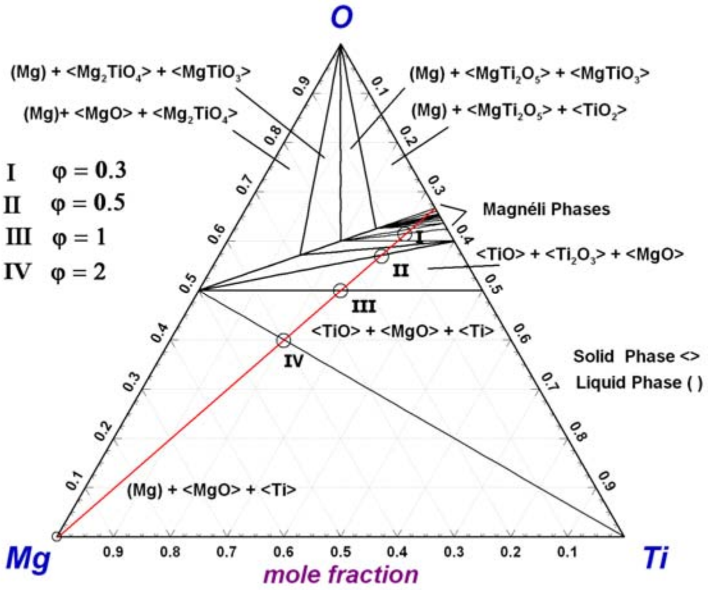

Figure 2: Ternary diagram Ti-Mg-O at 1000°C

It can be shown in an Ellingham diagram (Figure 3), that a reduction of high titanium oxide is more unfavourable than the reduction of TiO_2, since their free energy decreases considerably. The Gibbs free energy decreases about 0.83 times, when the reduction of TiO to metallic Ti is compared with the reduction of TiO_2. In the case of a reduction from the low end Magnéli phases (Ti_4O_7), the decrease of free energy is only about 0.38 times. The Ellingham diagram shows that reduction of any titanium oxide with magnesium below 1400°C is thermochemically favourable, since there are no energy barriers to avoid its complete reduction but the reduction of high titanium oxides is energetically more difficult than Magnèli Phases or TiO_2. At temperatures higher than 1400°C no metallic Titanium, only TiO can be produced.

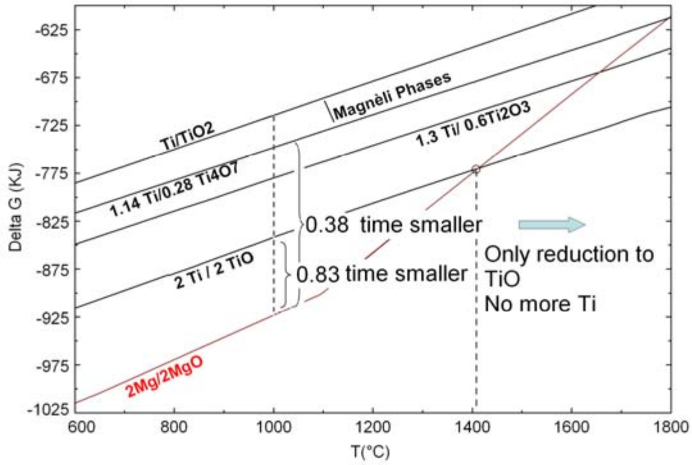

Figure 3: Ellingham diagram for titanium oxide

2.2 Structure of titanium oxides (phase transformation)

The phase transformation between the different titanium oxides depends on its difficulty to rebuild a new structure from the previous one. Crystalline structures of each titanium oxide can be seen on Table 1. Reduction from TiO_2 to Ti_2O_3 is relatively "easy" because the "rutile" structure is preserved and transformations do not need to be completely reconstructive. All Magnéli phases consist of slabs of a rutile structure, their width is dependent on the phase composition, separated by oxygen-deficient shear planes. Ti_2O_3 and the higher-oxide phases have atomic structures formed from corner-, edge-, and face-sharing TiO_6 octahedra, which can be basically created by regular shearing of the original rutile lattice. But the transformation from Ti_2O_3 to TiO is "difficult" because TiO has a face-centred cubic NaCl crystal structure, although with vacancies that are always present in a high concentration, and that are sometimes ordered on a superlattice creating a monoclinic modification of the cubic phase. TiO is not only much denser than the higher oxides, since most of the 6-fold coordinated interstices between oxygen atoms are occupied by titanium atoms, but also cannot be created by a simple shearing of the Ti_2O_3 lattice. Thus to form TiO, the lattice must be completely reconstructed [12]. This reconstruction presents a slow kinetic step or a kinetic barrier depending on the process conditions.

Table 1: Crystalline structure and colour of each titanium oxide [12],[14].

Oxidation State		% O wt	Crystal structure	Colour
	TiO_2	40.03	Tetragonal	White
Magnéli phases	$Ti_{10}O_9$ to Ti_4O_7 Ti_nO_{2n-1} $4 \leq n \leq 10$	37.5 – 36.8	Triclinic	$Ti_{10}O_{15}/Ti_7O_{13}$- Dark grey, Ti_6O_{11}/Ti_4O_7 - Dark blue
High titanium oxide	Ti_3O_5	35.75	α, β, γ Monoclinic	α – Dark blue β, γ – Dark red
	Ti_2O_3	33.36	β Rhombohedra – α HCP	Purple
	TiOx 0.7 < x < 1.3	20.7 – 11.2	α Monoclinic – β Cubic – γ CCC	γ Gold
Solid solution	TiO_x X<0.7	< 11.2	HCP	Silver

2.3 State of the art in magnesiothermic Ti-reduction processes

Within the last fifty years, there have been several attempts to use magnesium as deoxidiser or reducer medium for titanium dioxide. Titanium powder (different size, 4 wt % max. oxygen content) or titanium wires have been deoxidised using magnesiothermic methods by

Kubaschewsky [15] and Miyazaki [11] respectively. Deoxydized titanium with 1.8% to 2.8 wt % oxygen content was obtained, but the results by both researchers (Figure 4) do not show any correlation, their tendency lines are quite opposite.

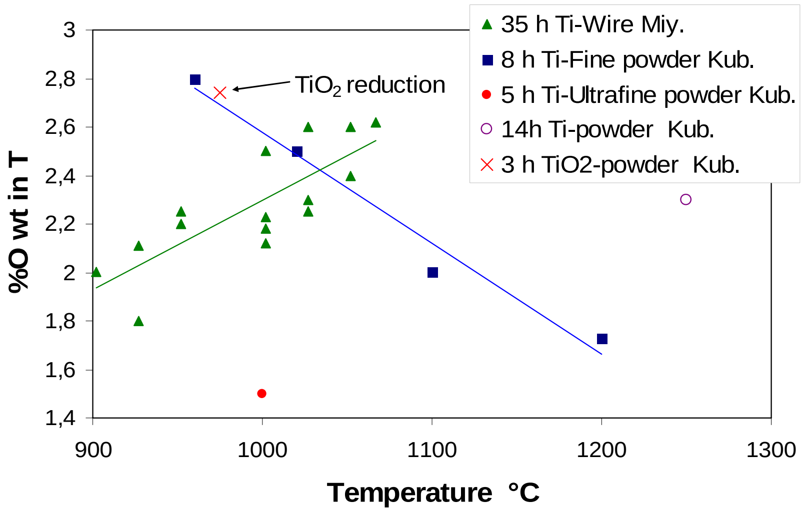

Figure 4: Oxygen content reached in magnesiothermic titanium deoxidation [11][15]

Magnesiothermic reduction of TiO_2 powder has been carried out by Kubaschewky and Rostron [17],[18]. Kubaschewsky obtained titanium with 2.8 wt % oxygen content (Figure 4) but Rostron obtained only products with 90 wt.% of titanium or high titanium oxide. A large scale experiment of 8.55 Kg was performed by Henrie [19], who used both magnesium and $MgCl_2$ in different ratios and two different gases, hydrogen and argon. Titanium metal with 2.3 wt % oxygen was obtained, when hydrogen, 30% wt $MgCl_2$ as protector-reducer gas and flux respectively were used.

2.4 Proposed process for Ti-powder production

The proposed process should obtain titanium powder avoiding the possible residual chlorine contents in comparison to other processes [7]. Furthermore, the necessary steps to produce titanium powder could be reduced by the proposed process using TiO_2 as raw material, in comparison to the current processes that use metallic titanium ingots. Magnesiothermic reduction of titanium dioxide is considered to be the first step to obtain titanium with an acceptable oxygen content of <2%. Leaching is required afterwards to remove the formed MgO and any excess Mg. The acid solution (HNO_3-HCl_2-H_2O) should be the same as used conventionally by the Kroll process. An excess of magnesium or magnesium oxide must be recycled. The titanium obtained from this treatment (Figure 5) could be used as charge material for a subsequent treatment including final deoxidation by calciothermic treatment as proposed by Okabe [1] to produce low oxygen content titanium powder. Additional investigations must be performed to determine the finally oxygen content on the powder reach by calciothermic deoxidation.

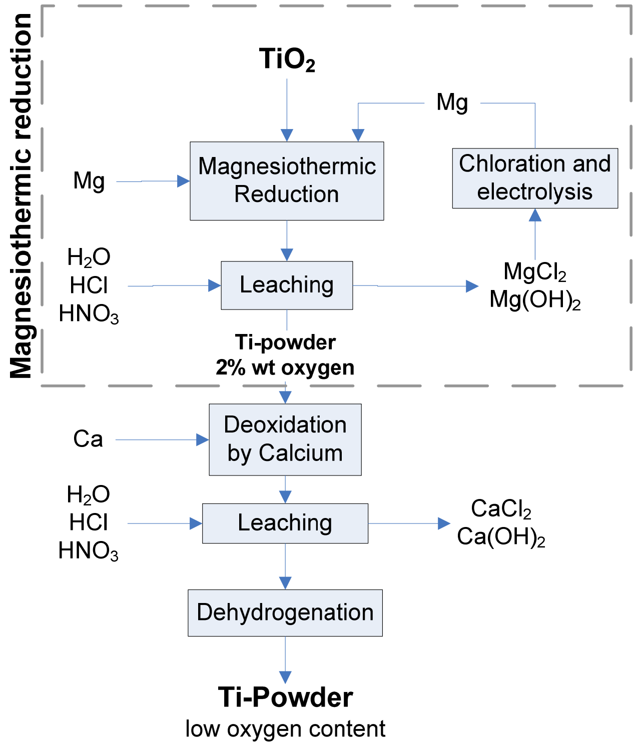

Figure 5: Proposed process to produce titanium powder by magnesiothermic reduction from Rutile.

The process window is limited by the following facts: The above mentioned thermochemical calculation show, that for temperatures higher than 1300°C, titanium is re-oxidised due to the increase of the partial pressure of O_2 in the relation Mg/MgO (Figure 6 left). The molar composition ratio φ must be higher than 2.5 (Fig 3) in order to keep the temperature under this critical value. The lowest oxygen content that can be reached by magnesiothermic reduction seems to be 2% wt as shown in the experimental data by Miyazaki (Figure 4) and φ should be even as high as 3.4 to achieve this value. Lower molar composition ratios will lead to higher process temperature and decrease the oxygen content (Figure 6 right). Energy losses were not considered for this calculation.

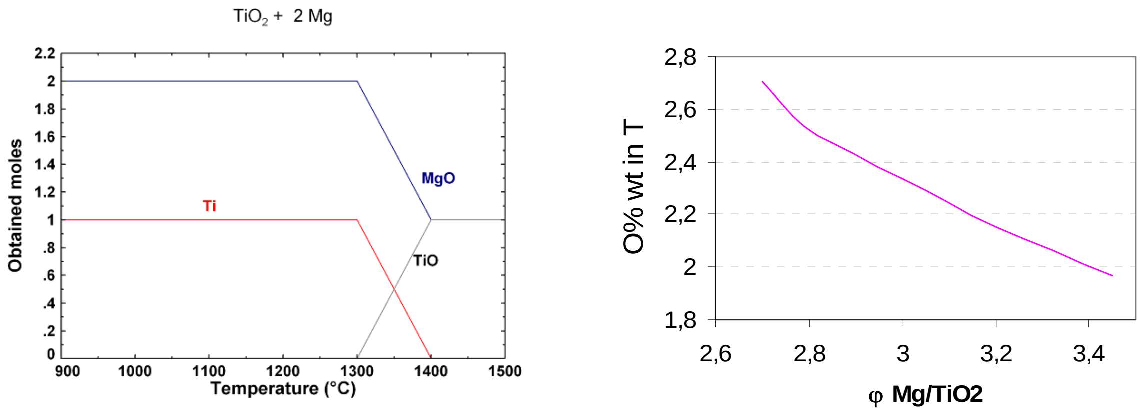

Figure 6: Left: mol quantity of phases present at different temperatures at $\varphi = 2$,
Right: dependence of oxygen content on the molar composition ratio.

3 Experimental set-up

The experiments were carried out using and pure magnesium of ≥ 99,9% wt and titanium dioxide powder “Kronos 3000” with the following properties: TiO_2 purity ≥ 99% wt, 86% of particles > 100 µm and 0,2% of particles < 800 µm, X_{50}-Value (media size particle) of 200 µm. A first experiment series was carried out in an reactor made of steel DIN 1.0402 (Vol 500 ml, Figure 7-left) with devices to measure temperature and to shield the reaction bed with gas (Ar flow up to 2 l/min) Argon was used as protecting gas for the external side of reactor too. An experimental design of 2^{4-1} variants with one replica (16 experiments, Table 2- 1.1 to 8.2) was implemented with the following variables/levels

(1) Magnesium shape: Cubes 20x20x20 mm and plates of 20 mm width
(2) Molar composition: $\varphi=2.5$ and $\varphi = 4$
(3) Particles size of TiO_2 powder: > 200 µm, <200µm
(4) Temperature: 720°C and 850°C.

The level of temperature was designed on the range where the self propagating reaction starts. Each experiment was carried out with 75 g of titanium dioxide and the amount of magnesium according to the experimental design. A velocity of heating at 12°C/min was set on the conductive heating device to reach 640°C, and then set to 3°C/min up to the target temperature. A holding time of 30 min was maintained when the target temperature was reached. At 400°C and 640°C the temperature was hold for 30 min to guarantee homogeneous heating throughout the whole powder bed. The change of temperature inside the bed was registered every second with a type K-thermocouple protected with alumina and later steel tubes. The test with the best results was repeated twice for reproducibility purposes.

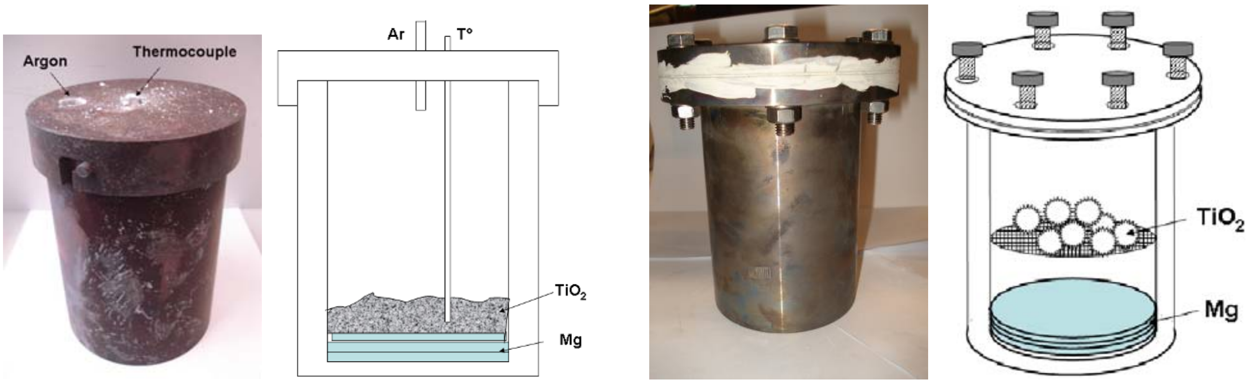

Figure 7: Left: Reactor 1 with device to measure temperature and gas;
Right: sealing reactor 2 of special steel to support 9.8 bar at 1000°C.

A second series of experiments was conducted using a sealed reactor (Vol. 350ml, Figure 7-right) made of heat resistant and high elevated-temperature strength steel DIN 1.4841 aimed to determine if a high reduction grade of products could be reached using magnesium vapour . Theoretically the magnesium partial pressure should increase continuously with the temperature. In all experiments argon was used (2 l/min) outside of reactor to avoid oxidation of the outer reactor walls. The reactor allowed holding a constant vapour pressure of magnesium during the process time in order to determine the influence on the grade of reduction reached. The reactor flange was coated with zirconium dioxide ZrO_2 to avoid its carburization because the gasket is made out of intercalated sheet of graphite-steel-graphite by Sigraflex Economy from SGL Group. Magnesium and titanium dioxide were separated with a stainless steel screen of 800 µm to ensure that only magnesium vapour contacts the TiO_2. 1g of titanium sponge was used in the reactor for gettering nitrogen gas. An experimental design of 2^3 variants without replicas (8 experiments) was implemented with the following variables level

(1) Holding temperature: 850°C and 1000°C
(to achieve different partial pressure of magnesium, 0.08 and 0.44 bar respectively)
(2) Holding times: 90 and 270 min
(3) shape of titanium dioxide: pellets > 1 mm and powder as received

The molar composition ratio was kept constant at $\varphi = 3$. Pellets were prepared with water to avoid contamination and dried at 200°C for 24 hours. A sufficient mechanical stabilization of the pellets was observed. A heating velocity of 12°C/min up 800°C, and then 4°C/min was used. When the target temperature was reached a holding time depending on the experimental design was maintained. At 400°C and 640°C the temperature was hold for 30 min to guarantee the same heating in all areas of the bed. An additional experiment to reduce the energy losses, the reactor was preheated externally to 580°C before of the starting temperature, and then rapidly introduced into the main furnace at 1100°C. The furnace temperature was decreased and maintained at 1000°C and kept there for 90 min.

After reduction, the recovered samples were analysed optically to determine roughly their reduction level. This was performed by dividing the material depending on their colour. According to Table 1, bright grey grains were considered as having a lower oxidation state from TiO_x $x<0.7$ to metallic Ti and dark grey grains as higher oxidation states from Magnéli Phases, titanates of magnesium or Ti_3O_5. Although visual colour evaluation can so roughly determine the influence of variables on the yield metal, it was enough to value the results obtained in this initial present research and determined possible mechanisms of the reaction. XRD analysis supported the theoretical correlation between colour and reduction grade. Some samples were analyzed by Optical microscopy, XRD, SEM and EDX.

4 Results and discussion

4.1 Reaction temperature

The starting point for the temperature increase was determined for all the tests on the reactor 1 to be at 660 ± 5°C, close to the melting temperature of magnesium (650°C) (Figure 8-right). This point can be considered the starting temperature of the reaction. The temperature measurements indicated that a strong exothermic reaction occurred generally in one single step, with a rapid increase and decrease of temperature inside the bed, while on its top the variation was not appreciable and stayed approximately the same as the furnace and the reactor top temperatures (Figure 8-left). In most of the experiments the maximum reaction temperature could not be measured exactly, because occasionally the protective alumina tube broke during the strong increase of temperature. Temperature measurements were quite different depending on the variables of the experimental design as Figure 8-right shows (tests 3 and 7 and their replica). When magnesium in plate form was used, the temperature increased more than when it was in cube form. That means the reaction was also stronger according to the percentage of high reduction grade products (Table 2). In all cases, a condensed magnesium layer was found afterwards on top of the bed (Figure 9-2), but the measured bulk temperatures never reached the boiling point of magnesium (1095°C), as shown on Figure 8. That suggests the reaction is heterogeneous with a local flash in temperature and a great temperature gradients inside the bed, depending on bed structure and particle characteristics. Due to this, there is no reproducibility in the shape of the curve as well as in the measured maximum temperatures.

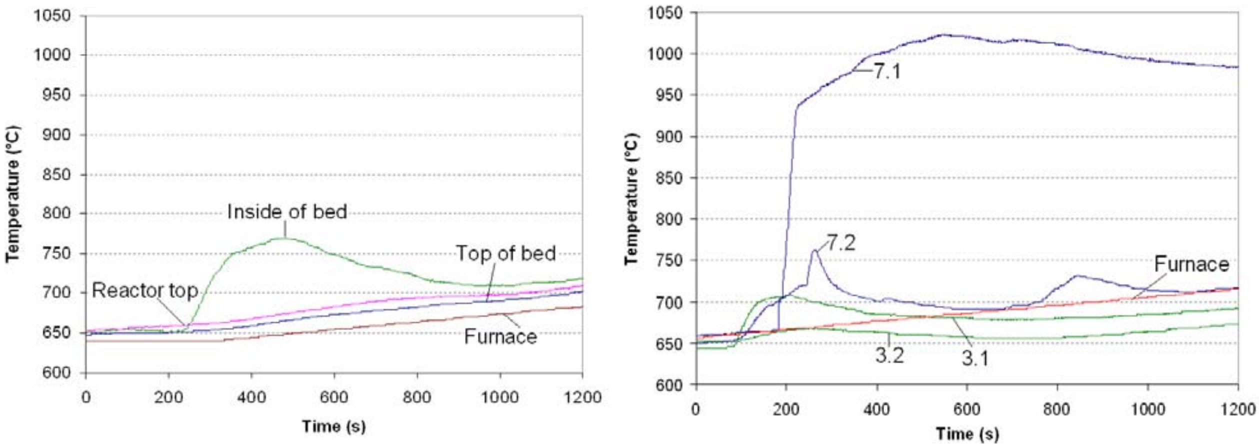

Figure 8: Right: Temperature measurement inside and on top of bed, in reactor top and furnace. Left: Test and its replica show no reproducibility on the higher temperature mesure of reaction (Reactor 1, Ar atmosphere)

4.2 Products and Reduction grades

A special products distribution was observed in the reactor 1, when Mg and TiO_2 were in contact. Distribution depends of the magnesium form used during the tests. One (See 4.3) Using analysis of this repetitive distribution, the starting temperature of the reaction, DRX, SEM and EDX, a descriptive mechanism of the reaction is proposed. In case of the plate form of magnesium, four different zones were observed Dark grey material was found at the bottom as loose grains and on the top of the bed as a sinter (Figure 9.3). Material of bright grey colour was observed only in the middle of the bed as a sinter (Figure 9.4). On the surface of all grains some detached small particles of MgO were always observed (Figure 12.a). Coloured grains (Ti_2O_3 or TiO) (Figure 9.4a) were hardly found. A layer of evaporated/condensed magnesium (Figure 9.2) was always seen on top of the bed in reactor 1. A coating with MgO was observed on top of the condensed magnesium layer in both reactors (Figure 9.1).

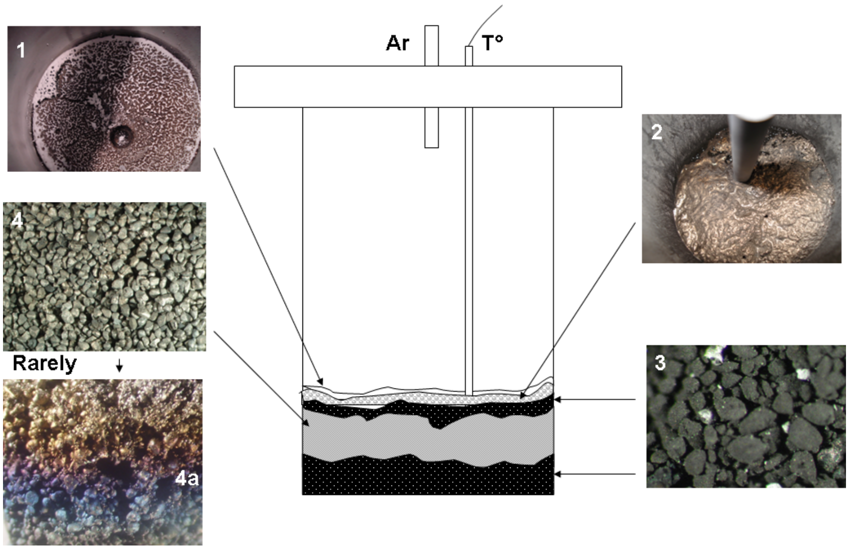

Figure 9: Product distribution inside the reacted material in reactor 1

Most of the reacted material after magnesiothermic reduction obtained in reactor 1 could be easily separated in two parts, the first one were represented by dark grains and the second one by grey ones. The XRD patterns of the bright grey product (originating from test 9.1) show MgO, Ti and Mg as principal peaks and only Ti_2O as Ti-oxide phase (Figure 10).

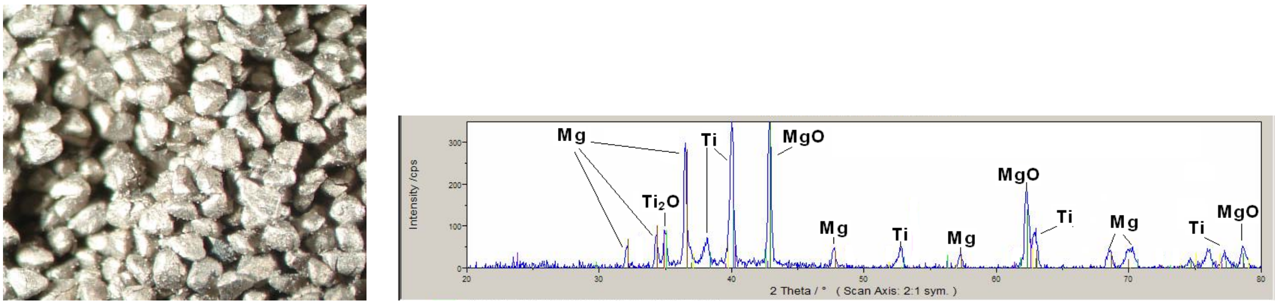

Figure 10: XRD patterns of the stronger reduced (grey) part of product

XRD patterns of the dark grey product (as example from test 4.1) show also Ti and MgO as the principal phase, but less reduced $Mg_{1.5}Ti_{1.5}O_4$, TiO_2 and Ti_2O_3 phases containing Ti (Figure 11).

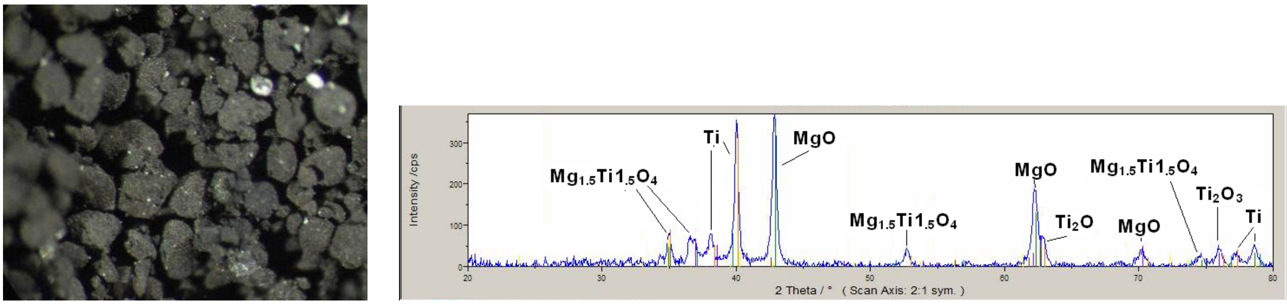

Figure 11: XRD patters of the weak reduced (dark grey) part of product

It can be concluded that the bright grey products are mainly formed of titanium and a little Ti_2O. They exhibit a high grade of reduction. Black grey products contain moreover $Mg_{1.5}Ti_{1.5}O_4$ and Ti_2O_3 and exhibit a low reduction grade. The methodology of optical assessment was used to receive a quick and qualitative judgement of the reduction grade. In order to remove remaining Mg-metal, the bright grey grains of test No. 9.2 were heated again in Ar-atmosphere (2 l/min) at 1100°C for about 2 hours. The XRD patterns now show only Ti_2O and MgO, and the colour remained the same. The following table shows the percentage of products obtained in the experiments carried out in the reactor 1.

Table 2: Results of experimental design 2^{4-1} each with two replicas and other additional experiment obtained in reactor type 1.

		Variables				%wt of Products					
Test No		Mg Form	Molar Ratio [φ]	TiO_2 added particle size µm	Temp. (max) [°C]	Ti-TiO High grade of reduction		Ti2O3-Magnéli Low grade of reduction		TiO_2 without reduction	
1.1	1.2	Cube	2.5	< 200	850	0	0	40	50	60	50
2.1	2.2	Cube	2.5	>200	710	0	0	60	80	40	20
3.1	3.2	Cube	4	< 200	850	0	0	90	85	10	15
4.1	4.1	Cube	4	>200	710	0	0	50	80	50	20
5.1	5.2	Plate	2.5	< 200	710	19	0	39	36	42	64
6.1	6.2	Plate	2.5	>200	850	24	50	14	16	62	34
7.1	7.2	Plate	4	< 200	710	83	78	16	23	0	0
8.1	8.2	Plate	4	>200	850	80	76	20	24	0	0
9.1	9.2	Plate	4	<200	850	70	85	30	15	0	0

Analysis of variance (ANOVA) has shown that the form of added magnesium had a strong influence on the reduction with a significance of 0.001. This value means there is a 99.9% probability that the magnesium form has an influence over the reduction grade. The molar composition ratio φ had less influence with a significance of only about 0.11 and the other two variables, temperature and particle size had an influence on reduction grade with a significance of only 0.73. The best experiment number 7.1-7.2 (reduction degree of 83-78%) was repeated and again a high reduction degree of about 70- 85% wt regarding Ti-TiO was obtained (9.1-9.2).

Unfortunately only low reduction degrees (100% dark gray material) were obtained in the second set of experiments using the sealed reactor when the reactive agent was separated with a screen. All studied variables (holding time, holding temperature and titanium dioxide shape) did not have any influence on the reduction yield, despite the fact, that almost all magnesium was evaporated and found condensed on the wall and on top of the reactor 2. Reduction within the pellets was homogeneous. Sometimes MgO blocked the screen and handicapped the free flow of magnesium, inhibiting the reaction, for which the test had to be repeated. An additional experiment with a preheated reactor 2, aimed on rapid evaporation of magnesium, obtained a low grade of reduction again. This result demonstrated that when a continuous increase of partial pressure of magnesium from 0 bar to 0.44 bar, exists the magnesium vapour reacts with TiO_2 to produce low grade reduction products. A kinetic barrier is induced as described on the next section. Currently another set of trials with Mg in contact of TiO_2 are being carried out with reactor 2.

4.3 Magnesiothermic reduction mechanism

When magnesium reaches the melting temperature, the liquid surface of magnesium (650°C) directly in contact with TiO_2 particles reacts and generates heat, forming reduced Ti-phases on the surface of the particle and MgO as a product either as detached small particles or inside the (pre-)reduced area of $Mg_{1.5}Ti_{1.5}O_4$ and Ti_2O_3 (Figure 12). The generated heat is immediately used to maintain the fusion of further magnesium metal. As more liquid magnesium is now available to react with TiO_2 this is a self propagating reaction. The generated heat increases the bulk temperature rapidly until exceeding the boiling point of magnesium, which then is quickly evaporated. The start of this process can be considered as a liquid-solid reaction. The first grains that have reacted with liquid magnesium reach only low reduction grades and can be found at the bottom of the reactor as loose grains. Further reduction of the grains is not easily reached, because it needs reconstruction of the crystalline structure from $Mg_{1.5}Ti_{1.5}O_4$ or Ti_2O_3 to Ti (see 2.2). This induces a kinetic barrier and reduces reaction speed although a high amount of magnesium vapour is already available. The reduction model can be considered similar as proposed by Alexander [12] on the electrochemical reduction of titanium dioxide in molten calcium chloride.

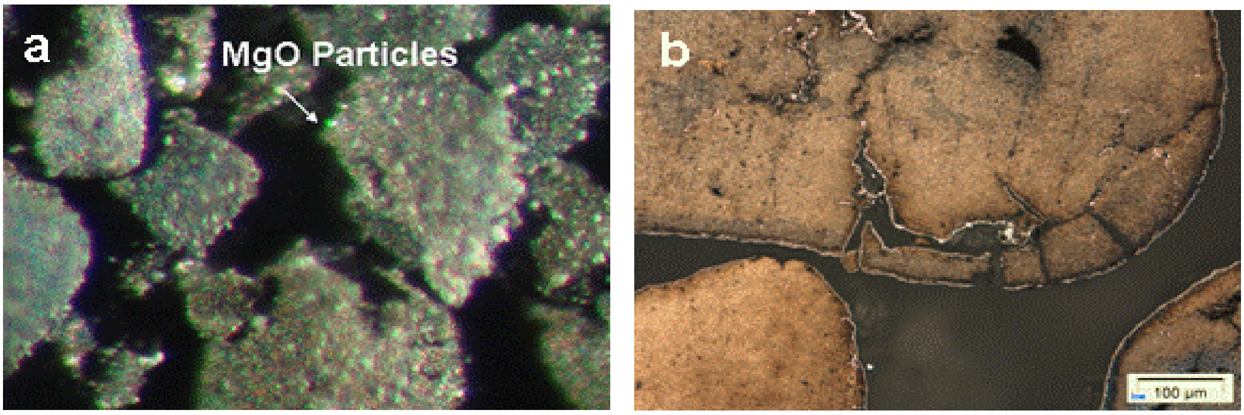

Figure 12: a) White: detached small particles of MgO on the surface of reduced grains
b) particles low reduction grade showing three different zones, a coating of Ti, a shell zone of MgO and the core area of magnesium titanates.

If magnesium plates are charged at the bottom of reactor, the generated vapour flows homogenously through the oxide bed. In this case a high grade of reduction can be achieved in the center of the reactor, due to sufficient local temperature and a high partial pressure of magnesium. In case of distributed magnesium cubes the vapour passes in channels leading to low reduction yields. When the vapour contacts the surface the TiO_2 particle, MgO is formed and partially removed by the gas stream as small particles. A thin MgO layer can be found on top of the bed. This reaction leaves a porous surface (core-shell) structure around the particle, through which magnesium vapour can pass inside for further reduction. Generated MgO now remains inside the particles and slightly impedes the flow of magnesium, resulting in Ti_2O-formation (Figure 13, Figure 14). The generated heat inside the particle flows outside, promoting migration of titanium from the middle to the outer zone and producing a separation between the MgO and Ti phases (Fig. 11). Grain edges exhibit a microstructure like a sinter, which confirmes that high temperature has been reached.

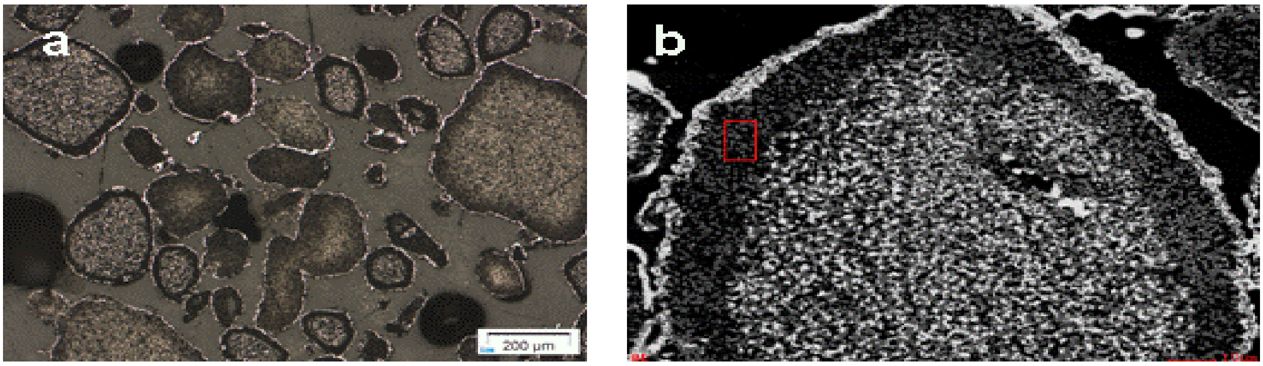

Figure 13: High grade reduction particles: a) Optical micrography, sintered shell of the particles;
b) SEM/EDX, bright external zone containing Ti, dark middle zone of MgO, and the core as mixture of Ti, MgO and Ti_2O.

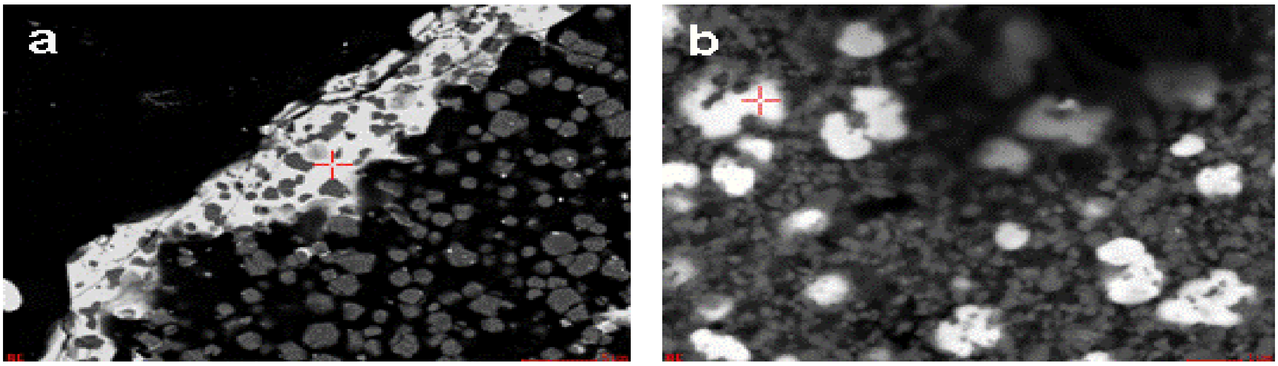

Figure 14: High grade reduction particles: a) SEM/EDX showing white coating of Ti mixed with black grains of MgO and middle zone only of MgO. b) Core zone with white grains of Mg or Ti and black MgO spots

Argon flows continuously inside the reactor on top of the bed and cools it down. Furthermore, the temperature of the furnace during the reaction is at maximum 700°C, because only few seconds have passed after the starting point of the reaction (660 ± 5 °C) and there is not enough time for heating (Figure 8-left). On top of the bed, vaporised magnesium is rapidly condensed forming a metallic layer due to the extreme heat loss. High flash temperature is confirmed by both the condensed magnesium layer on top of the bed and its absence at the bottom. The retention time on the top of the bed is too short to achieve a high grade reduction.

Experiments with continuous increase of partial pressure of magnesium were carried out in reactor 2, allowing for longer reaction time (max. 360 min). Despite the fact, that the system was perfectly sealed these tests always achieved a disappointing low grade of reduction, as described before. A continuously slow increase of vapour pressure can reduce the titanium dioxide only up to a low reduction grade, because there is not enough energy to overtake the kinetic barrier described above.

The formation of Magnéli phases or other high titanium oxides different to Ti_2O_3 can be considered as “intermediate reaction products” as they are not present in the obtained products. The kinetic barrier built up by the transformation of magnesium titanates or Ti_2O_3 to Ti can only be overcome if an extreme partial pressure of magnesium is maintained for a few seconds and at the same time local overheating is avoided. This may have happened in the middle of the reactor and seems to be the key factor to achieve high and homogenous reduction of TiO_2 to Ti.

5 Conclusions and Outlook

Experiments regarding magnesiothermic reduction of TiO_2 provided a mixed product of high degree of reduction (Ti, few Ti_2O) and low degree of reduction (magnesium titanates and Ti_2O_3) obtained in a special distribution inside the reactor. From different analysis, it is likely to conclude that high a grade of reduction is achieved when a spontaneous high partial pressure of magnesium appears during a few seconds. A slow and continuous increase of the Mg partial pressure led to the formation of magnesium titanates and to a kinetic barrier that impeded a subsequent reduction to metallic titanium. Previous experimental data have shown that it is possible to achieve oxygen contents of about 2.2 % wt, but the current laboratory scale set-up did not allow to obtain such values. The key to obtain a high grade of reduction shall be accomplished by means of a continuous reactor design considering magnesiothermic reduction as a gas-solid reaction with the option to supply high magnesium vapour pressure abruptly. The easiest way to control temperature is to use an over-stoichiometric amount of magnesium bearing in mind to keep the process temperature below 1300°C. These issues shall be matter of further research at IME, in order to determine the technical feasibility of producing titanium powder using this route.

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