Rafael Bolívar León

Synthesis of titanium powder by magnesiothermic reduction from titanium dioxide

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RWTH AACHEN UNIVERSITY

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Aachen, February 6th 2018 Rafael Bolívar León

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Resume

In the last two decades a research race began to obtain low cost titanium powder directly from both titanium dioxide (TiO_2) or tetrachloride ($TiCl_4$) in order to reduce the final cost of manufactured components and increase the market penetration. Unfortunately, nowadays, there is no industrial scale up for these processes to assure a massive production of titanium powder. The aim of this research was to study a process to obtain titanium powder (2.9 wt% O) by magnesiothermic reduction of TiO2. The research included (1) a thermochemical simulation of the reaction to find the window process of the variable; (2) a design of three different reactors which promote solid-liquid and solid-gas model reaction and permit the analysis to determinate variables; (3) 89 metallothermic reductions experiment to evaluate the influence of time, temperature, molar ratio of Mg/TiO_2, size of TiO_2 and shape of magnesium; (4) 14 leaching processes of products by different mixtures of acid to evaluate purification of solid titanium metal by dissolution of Mg, MgO, Ni, Fe, magnesium titanates and titanium oxides; (5) a pathway of the magnesiothermic reaction to explain the results of the experiment and the reaction. The behaviour of the reaction depends on the type of reactor used. If the reactants are placed with each other, at the magnesium melting temperature (660°), the reaction starts and becomes a self-propagating behaviour. A huge exothermic reaction is evolved and the entire amount of magnesium is evaporated in an abrupt flash of temperature increase .Frequently, an engulfed titanium layer was observed on the particle surface. This layer blocked the flow of magnesium inside the particle acting as a physical barrier. Additionally, a thermochemical barrier was observed during the reduction, due to the transformation from Ti_2O_3 to TiO that requires a complete crystal reconstruction. If the reactants are placed separately and a rotary movement is used on the reactor, the reaction runs quietly permitting control of temperature and avoiding the reoxidation of the obtained titanium. A high yield of titanium metal is obtained. The most important conclusions of this work are (1) the high yield of titanium metal is achieved when a solid-gas reaction in a rotary movement of the reactants is promoted; (2) the control of temperature is a sensible parameter because at temperatures higher than 1400°C a reoxidation of the titanium is present; (3) the type of reactor was the key to obtain high yield of titanium powder; (4) the sealed and rotary tube reactor with two compartments in which magnesium and TiO_2 powder were placed separately was the best configuration; (5) the mixture of 8 HCl% + 3 HNO_3% at 20°C in 24 hours promotes the highest dissolution of sub-products and the lowest of titanium metal; (6) irregular and semispherical particles of powder sizes between 5 to 20 µm were obtained.

Zusammenfassung

In den letzten zwei Jahrzehnten begann ein Forschungsrennen damit, kostengünstiges Titanpulver direkt aus Titandioxid (TiO_2) oder Tetrachlorid ($TiCl_4$) zu erhalten, um die Endkosten der hergestellten Komponenten zu reduzieren und die Marktdurchdringung zu erhöhen. Leider gibt es heutzutage keinen industriellen Maßstab für diese Verfahren, um eine massive Produktion von Titanpulver zu gewährleisten. Das Ziel dieser Forschung war es, ein Verfahren zur Gewinnung von Titanpulver (2.9 Gew -% O) durch magnesiothermische Reduktion von TiO_2 zu untersuchen. Die Untersuchung beinhaltete (1) eine thermochemische Simulation der Reaktion, um den Fensterprozess der Variablen zu finden; (2) ein Entwurf von drei verschiedenen Reaktoren, die die Fest-Flüssig- und Fest-Gas-Modellreaktion fördern und der Analyse ermöglichen, Variablen zu bestimmen; (3) 89 Experiment der metallothermischen Reduktion, um den Einfluss von Zeit, Temperatur, Molverhältnis von Mg/TiO_2, Größe von TiO_2 und Form von Magnesium zu bewerten; (4) 14 Auslaugungsprozesse von Produkten durch verschiedene Mischungen von Säure zur Bewertung der Reinigung von festem Titanmetall; (5) einen Weg der magnesiothermischen Reduktion, um die Ergebnisse des Versuchs und die Reaktion zu erklären. Das Verhalten der Reaktion hängt von der Art des verwendeten Reaktors ab. Wenn die Reaktanten bei der Magnesiumschmelztemperatur (660°) miteinander platziert werden, beginnt die Reaktion und wird zu einem sich selbst ausbreitenden Verhalten. Eine riesige exotherme Reaktion wird entwickelt und die gesamte Menge an Magnesium wird verdampft in einem plötzlichen Temperaturanstieg, aber das entwickelte Titan wird reoxidiert. Häufig wurde eine eingehüllte Titanschicht auf der Partikeloberfläche beobachtet. Diese Schicht blockierte den Magnesiumfluss im Inneren des Partikels als physikalische Barriere. Zusätzlich wurde während der Reduktion eine thermochemische Barriere beobachtet, die auf der Umwandlung von Ti_2O_3 in TiO beruht, die eine vollständige Kristallrekonstruktion erfordert. Wenn die Reaktanten getrennt angeordnet werden und eine Drehbewegung am Reaktor verwendet wird, läuft die Reaktion ruhig ab, was die Temperaturkontrolle erlaubt und die Reoxidation des erhaltenen Titans vermeidet. Es wird eine hohe Ausbeute an Titanmetall erhalten.Die wichtigsten Schlussfolgerungen dieser Arbeit sind: (1) der hohe Ertrag an Titanmetall wird erreicht, wenn eine Festgasreaktion bei einer Drehbewegung der Reaktanten gefördert wird; (2) die Kontrolle der Temperatur ist ein sinnvoller Parameter, da bei Temperaturen von mehr als 1400 ° C eine Reoxidation des Titans vorliegt; (3) der Reaktortyp war der Schlüssel, um einen hohen Ertrag an Titanpulver zu erhalten; (4) der versiegelte und Drehrohrreaktor mit zwei Kompartimenten, in denen Magnesium und TiO_2 -Pulver getrennt angeordnet waren, war die beste Konfiguration; (5) das Gemisch aus 8 HCl% + 3 HNO_3 3% bei 20 ° C in 24 Stunden fördert die höchste Auflösung von Nebenprodukten und die niedrigste Auflösung von Titanmetall; (6) unregelmäßige und halbkugelförmige Teilchen mit Pulvergrößen zwischen 5 und 20 µm wurden erhalten.

Extended Abstract

In the last two decades the research race began again to obtain low cost titanium powder directly from its titanium dioxide (TiO_2) or tetrachloride ($TiCl_4$). Electrochemical processes to obtain titanium powder from TiO_2 by reduction through melting calcium or its salts had been researched at the same time by Susuky [56] [57] and Fray (FFC process) [58] [59]. The Kroll and Hunter processes have improved to produce continuous titanium powder made by the Australians (TiRo™ process) [60] and the American (Armstrong ITP Process) [61] respectively. Okabe [62] investigated the direct production of titanium through calciothermic reduction of TiO_2. Unfortunately, nowadays, there is no industrial scale up for these processes to assure a massive production of titanium powder at low cost.

The proposed four step process (Figure I) consists in a first reduction of titanium dioxide by magnesium to low titanium oxygen content minimum of 2.9 wt%, following an acid leaching step to recover the powder which is used as raw material in a subsequent calcium deoxidation process. Finally, another acid leaching step would obtain the low oxygen content titanium powder. The requirement of the oxygen content depends on the application where the component will be used. Possible new daily applications could use titanium with higher oxygen content than that commonly used in high technical application which gives high range on the process control.

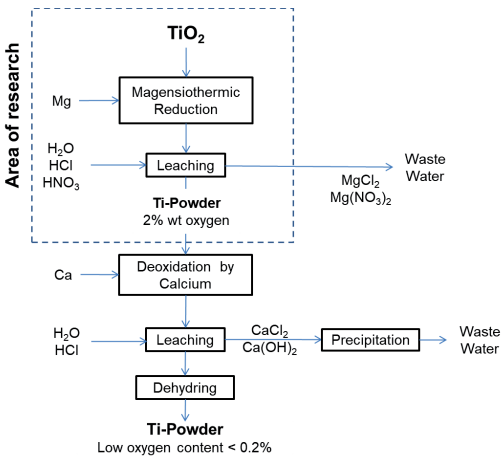

Figure I: Proposed process to produce titanium powder by magnesiothermic reduction from Rutile.

Physicochemical Background of Magenesiothermic Reduction

The magnesiothermic reduction can be represented by the following theoretical equation:

$$\frac{1}{2}TiO_2 + Mg \rightarrow \frac{1}{2}Ti + MgO \qquad \text{(I)}$$

This non-self propagating exothermic reaction exhibits an enthalpy of -129.1 kJ/mol, an adiabatic process temperature of 1814°C and Dautzenberg parameter of 2009 J/g. Reactions with the Dautzenberg parameter higher than 3000 J/g should be self-propagating [109].

Figure II shows ternary FactSage® 6.1 calculated diagrams at two different temperatures, 1000°C and 1400°C. In these diagrams it can be noted that at a higher temperature (1450°C) it is not possible to obtain metallic titanium as the only product; instead a mixture of titanium and titanium oxides is obtained. To understand the reaction progress, a connection line between Mg and TiO_2 was traced in both diagrams to show the possible equilibrium phases existing with variation of the molar composition ratio (φ), which can be described using the following equation:

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

Where η represents the mol number of each component.

Three and four points are presented in the diagrams at 1450°C and 1000°C. On the 1000°C diagram (Figure II), at low magnesium ratios ($\varphi < 0.3$) are formed both 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 ($\varphi<0.5$) the formation of magnesium titanates no longer occurs and instead MgO is formed. Metallic titanium has been obtained for the first time in a mixture of TiO and MgO within the range between points III and IV ($1<\varphi<2$). Beyond point IV, TiO was transformed into metallic titanium, while both magnesium oxide and the excess of magnesium retained their metallic form.

At the 1450°C diagram (Figure II), the behaviour of the reaction is the same up to point 3, since at this temperature point 4 disappears; no more

reduction is possible and only a mixture between TiO and MgO. The diagram shows a region where metallic titanium is present, but with TiO and MgO.

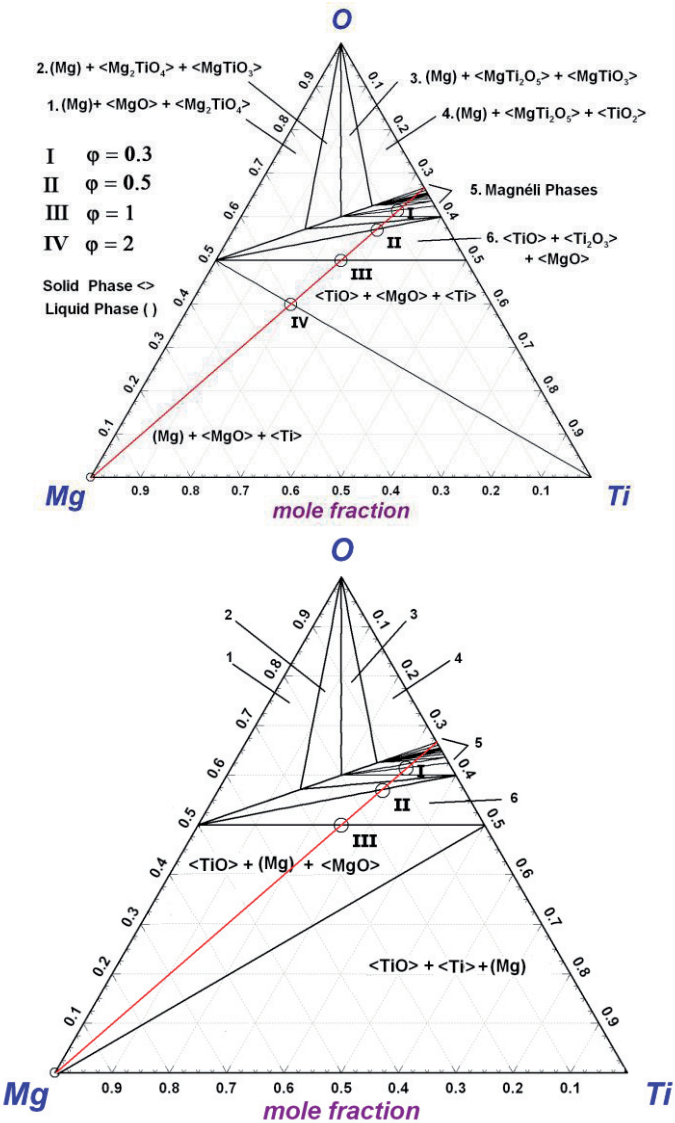

Figure II: Ternary diagram Ti-Mg-O up at 1000°C, down at 1450°C calculated by FactSage® 6.1.

At a temperature of 1450°C there is no possibility to obtain a complete reduction to metallic titanium. The percentage of the theoretical amount of each product can be calculated using the ternary diagram. For example, at a φ = 2 (point IV) the molar fraction percentage of the obtained titanium is only 20 mol% (or 37.3 wt%) of the total product; the rest is constituted by MgO. Magnesiothermic reduction will always obtain a huge amount of MgO, at least 80 mol% (62.7 wt%), in comparison to the metallic titanium. Approximately of this 80 mol% is half the quantity; 40 mol% (24.9 wt%) belongs to oxygen and the other one 40 mol% (37.8 wt%) to the magnesium. Additionally, the MgO must be separated by subsequent treatments, such as leaching. At high temperatures, the partial pressure of oxygen on the reaction of Mg/MgO increases leading to a reoxidation of the titanium as shown in the Ellingham diagram- calculate using both FactSage 6.1 and data for the solid solution of oxygen in titanium $Ti_{[O]}$ [122].

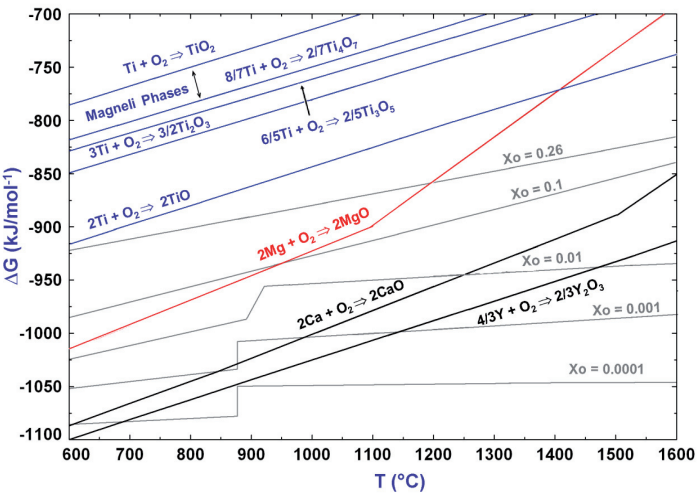

Figure III: Ellingham diagram for titanium oxide and fraction molar (Xo) of dissolved oxygen in titanium calculated by FactSage® 6.1.

Figure III shows that a complete reduction of all titanium oxides with magnesium is thermochemically favourable at temperatures below 1400°C since there are no energy barriers to avoid its complete reduction. At temperatures higher than 1400°C metallic titanium would not obtained, only TiO. The ΔG of the magnesium oxidation reaction (-725 kJ/mol) overcomes that of titanium oxidation. A reduction of magnesium oxide by me-

tallic titanium takes place, leading to the re-oxidation of titanium to titanium suboxide (TiO). The X_o represents the mol fractions of oxygen dissolved in titanium. Figure III shows that below 1200°C it is thermochemically possible to obtain titanium with Xo=0.26 of oxygen content (10.5 wt% O) and below 950°C, titanium with Xo=0.1 oxygen content (3.58 wt% Oxygen). The rough change on the slope of some lines of $Ti_{[O]}$ represents the different solubility of oxygen when titanium is transformed from the CCC cell to HCP cell or, in other words, from α-titanium to ß-titanium. However, this calculation disagrees with the experimental data which reported that at 1000°C titanium with 2.3 wt% O (Xo=0.066) was obtained when a reduction of titanium dioxide and magnesium was carried out [55].

Process temperature

The adiabatic process temperature is defined where the difference between the enthalpy of products in equilibrium at the process temperature and the enthalpy of reactants in equilibrium at the start temperature is zero [123]. During magnesiothermic reduction, the reached reduction degree depends on the maximal temperature achieved during the process (Figure IV) which depends itself on two factors. The first one is the liberated energy during the reaction which depends in turn on the molar composition ratio φ of reactive agents. The second one is the energy loss by conduction, convection or radiation through reactor walls but it was neglected in this calculation. The maximal process temperature resulted from the calculation at a molar composition ratio of $\varphi = 2$ and at a starting temperature reaction of 25°C, 650°C or 1094°C, these were 1814°C, 2423°C and 2721°C respectively. The theoretical stoichiometric proportion to satisfy the magnesiothermic reaction (Equation I) is a molar ratio $\varphi = 2$. Theoretically, this condition generates enough energy (process temperature calculate was 1813°C) to evaporate the whole magnesium bulk and to melt the evolved titanium metal. However, at this temperature, titanium metal would re-oxidize and only titanium oxide will be obtained. A molar composition ratio of $\varphi \leq 2.7$, $\varphi \leq 3.42$ and $\varphi \leq 3.9$ at a start temperature of 25°C, 650°C and 1094°C respectively, could generate enough energy to evaporate the bulk magnesium available in the reaction mix. Higher molar composition ratios (an increase of the magnesium amount) reduces the process temperature because the generated energy must be employed for both the necessary transformation phases during the reduction and to transform the magnesium excess into the equilibrium phase (Figure IV). Theoretically at higher temperatures than 1400°C (easily achieved as the process temperature) a re-oxidation of the obtained titanium will take place but the cooling on equilibrium conditions

leads to a reduction of Ti from its sub-oxide. The experimental validation of this (thermochemical) statement is one of the aims of this investigation.

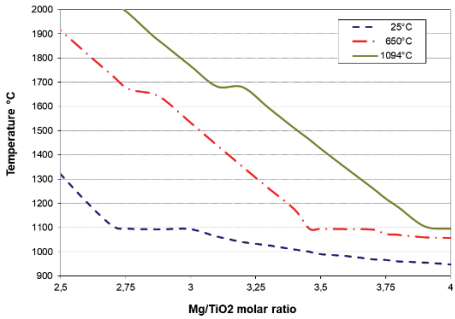

Figure IV: Adiabatic process temperature versus the increasing molar composition ratio at different starting temperature reaction (25°, 650° and 1094°C) calculated by FactSage® 6.1.

Set up and Results of the Experimental Work

The experiments were carried out using pure magnesium of ≥ 99.9 wt% and titanium dioxide powder "Kronos 3000" with the following properties: TiO_2 purity ≥ 99 wt%, size distribution 86 wt% of particles > 100 µm and 0.2 wt% of particles < 800 µm, X_{50}-Value (media size particle) of 200 µm. The studied variables were 1) temperature, 2) molar composition ratios φ, 3) sizes of TiO_2, 4) shape of Mg, 5) reaction time and 6) kind of reactor. The reactors were heated by electrical furnace with facilities to inject argon as the protective gas. Three different reactors were used in order to provide the possibility to investigate the mechanism reaction, as follow:

Reactor I

The first reactor (RI) was made of normal carbon steel DIN 1.0402 (Figure V) with a capacity of 500 ml and some gadgets on top for temperature measurement and protective gas injection. Argon (2 l/min) was injected into both the reactor and the furnace during the experiments. Magnesium (95 g) in different shapes (in cubes, plates or turnings) and titanium dioxide powder (the amount depends on the molar ratio, labelled "φ"). These were always placed in contact with each other within the reactor. Magnesium was generally placed at the bottom and then TiO_2 was poured on top of it.

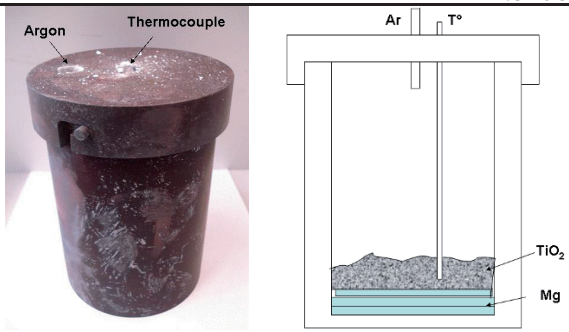

Figure V: Reactor I (RI) with facilities to inject protective gas and to measure temperature.

In reactor I three different experimental series were conducted. The assessment criterion was the grade of the reduction which was valued by the amount of the strongly reduced product obtained. The first experimental series was a normal experimental design where the following variables were changed: (1) the shape of magnesium as turnings, plates (20 mm wide) or cubes (20*20 mm) and (2) the molar ratio φ switched on 2.5 or 4. The set parameter were at the temperature (850°) and the size of TiO_2 powder (as received). The second one was a 2^{4-1} fractional factorial experimental design. The variables were (1) magnesium shaped in cubes or plates, (2) molar ratio φ (2.5 or 4), (3) particle size of TiO_2 (+200 μm or -200 μm) and (4) set temperature (710°C or 850°C). Holding reaction time of 30 minutes was always maintained constant. The last experimental series was again a normal experimental design where only the shape of the magnesium (cubes or plates) was changed. The other parameter, such as particle size of TiO_2 (>355 μm), molar ratio (φ = 4), temperature (850°C) and holding reaction time (30 min) were maintained constant. One replica of each trial was always carried out in order to obtain a minimum statistical concordance [124]. For each experimental series carried out on the different reactors, an analysis of variance was calculated in order to identify the influence of the dependents variables on the degree of reduction.

Reactor II

The second reactor (RII, Figure VI) was built with high elevated-temperature strength stainless steel DIN 1.4841. The 500 ml capacity reactor could support a pressure of 9.8 bars at 1000°C. The reactor was sealed by a blind flange, screws and a gasket seal. Sponge titanium lumps were

placed as getter into the reactor, in order to remove the enclosed air by forming titanium oxides and nitrides.

Figure VI: Sealing reactor II of special steel to support 9.8 bars at 1000°C.

Two different experimental series were implemented the using factorial experimental design. The first one was a 2^{4-1} fractional factorial experimental design. The reagents were in contact with each other. Magnesium was added as plates and TiO_2 as different sized powders. The variables studied were: (1) particle size of TiO_2 powder (as received or +355 μm), (2) molar ratio φ (2.5 or 4), (3) set temperature (850°C or 1000°C) and (4) holding reaction time (30 or 360 min) which was chosen as the confuse variable. Magnesium (75 g) in plate shape was always used. The amount of titanium depended on the molar ratio.

The second experimental series was a 2^{3-1} fractional factorial experimental design. The aim of this experimental series was to determine the influence of the increase of partial pressure of magnesium gas on the grade reduction when TiO_2 and Mg were placed separately and only Mg vapour could react with the titanium dioxide. The chosen variables were (1) shape of TiO_2 (powder >255 μm or pellets > 1 mm), (2) holding reaction time (90 or 240 min) and (3) temperature (850°C or 1000°C). No binder was used to obtain the pellets. The mechanical stability was achieved as TiO_2 was dipped and dried (150°C during 24 hours) with the advantage of external contamination avoided. In order to separate the reagents, a mesh of stainless steel was used. At the beginning, a stainless steel mesh of 200 μm opening was used, but it was frequently blocked by the evolved MgO. These results were rejected. To avoid this problem, the mesh was replaced by an 800 μm; thus, it made it impossible to keep on using TiO_2 powder.

Reactor III

The last (RII, Figure VII) design was a tube reactor formed by two different compartments joined by a joint flange in-between (Figure VIII). Each compartment had a capacity of 350 ml. It was made from high elevated-temperature strength stainless steel DIN 1.4841. The reactor was sealed on its ends with blind flanges and screws made out of the same material. A gasket of “Sigraflex® Economy” was used as well. The reactor was designed to support pressure of 9.8 bars at 1000°C. It was heated in a rotary furnace (2 rpm) with facilities to inject argon (2 l/min) as protecting gas.

Figure VII: Third Reactor formed with two compartments. It could support a pressure of 9.8 bars at 1000°C.

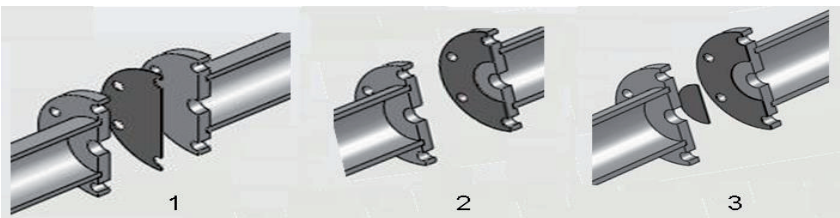

Figure VIII: Different configuration for Reactor III.

On the first configuration/experimental series, an experimental design 2^2 with two repetitions was implemented. Variables were (1) the molar ratio (2.5 or 4) and (2) holding reaction temperature (850°C or 1100°C). The size of titanium dioxide (as received) and the holding time (240 min) were maintained constant. For the second one, reagents were placed independently in each compartment (TiO_2 200 g). The hole allowed free flow of the magnesium vapour from the magnesium compartment to the TiO_2 compartment during the entire heating time. Set up temperature of 1100°C was maintained during 240 min. For the last configuration/experimental series; the compartments were isolated and the TiO_2 (200 g) and Mg were placed separately for each one. A special design of graphite gaskets made from Sigraflex® Economy was placed in-between the joint flanges. They allowed arranging a special blind plug of nickel, which blocked up the flow of magnesium vapour between both compartments

until it had melted due to a reaction with the vapour magnesium. Since the evolved nickel-magnesium alloy was melted, the magnesium vapour at approximately 0.58 bar, abruptly flowed into the TiO_2 compartment and began the reaction. Four trials were carried out at the set temperature of 1100°C with a holding time of 240 minutes.

Products of the Magnesiothermic Reduction

Five kinds of particles grouped of different grades of reduction and commonly grouped in the form of sinter cake or placed on a specific place of the reactor. These were obtained during the reduction from different conditions studied. Grey strong reduced particles, black metallic intermediate reduced, black no metallic weakly reduced, no reduced TiO_2 and another one. The strong and intermediate reduced particles are called SRP (strongly reduced product) and the weakly one is WRP (Weakly reduced product). Those products, also SRP and WRP were obtained alone or as a mixture, depending on each particular configuration in the trial. They can be separated by hand and classified by it colour and texture, and were analysed by ICP, XRD, SEM, EDX and optical microscopy. The other products were the sub-products of the magnesiothermic reduction; such as, MgO, $MgHN_3$. Titanium dioxide without any reaction was observed as well. The last one was hardly observed.

Strongly reduced product

The strongly reduced products (SRP) exhibit two different colours. The first one is grey silver in the particles which form a sinter-cake of metallic appearance and is obtained in trials where the reagents are place in contact with each other or separately. The second one is a black metallic detachment powder produced in trials where the reagents were placed separately and only a gas-solid reaction was allowed to run.

<u>The grey strongly reduced product</u>: High amounts of the grey metallic appearance of the strongly reduced product (Figure IX) were obtained in all of the following: RI when magnesium plate was used and the molar ratio of 4; RII when TiO_2 particles greater than 355 μm were used and RII when the reagents were in contact with each other. The highest amount of the strongly reduced products (85.2 wt%) was obtained for the sample RI-152 and carried out in the molar ratio of 4, particle >200 μm with a temperature of 850°C. The grey strongly reduced product is formed by silver in the particles which form a sinter-cake of metallic appearance and is obtained in trials where the reagents are in contact with each other. XRD pattern (Figure IX) shows metallic titanium (Ti), a low proportion of

sub-oxide (Ti_2O), magnesium oxide (MgO) and metallic magnesium (Mg). The second one is a black metallic detachment powder produced in trials where the reagents were placed separately and only a gas-solid reaction was allowed to run. The strongly reduced particles exhibit a singular morphology for three different zones: One external coating of metallic Titanium, a middle dark zone of MgO and a mixed inner zone of MgO and Ti_2O determined by SEM and EDX (Figure X).

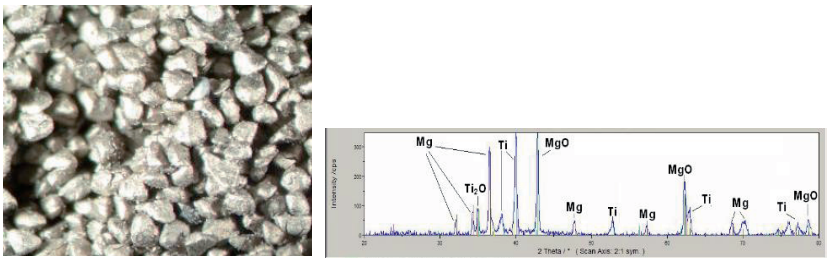

Figure IX: Grey strongly reduced product and its XRD patterns.

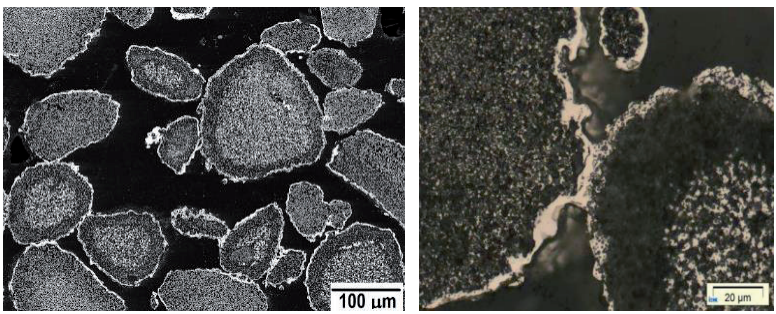

Figure X: Grey strongly reduced product: a) SEM micrography, sintered shell of the particles; b) SEM/EDX, bright external zone containing Ti, dark middle zone of MgO, and the core as mixture of Ti, MgO and Ti_2O.

<u>The metallic black strongly reduced product</u>: In the other cases, when the reagents were separated, the particle exhibits a homogeneous structure on the whole surface. A mixture between the titanium and magnesium oxide can be observed. The evolved coating of metallic titanium hinders the continuous supply of magnesium gas into the core resulting in a physical barrier for total reduction of TiO_2, leading to a partial reduction to produced low amounts of $Mg_{1.5}Ti_{1.5}O$, Ti_2O and Ti_2O_3.

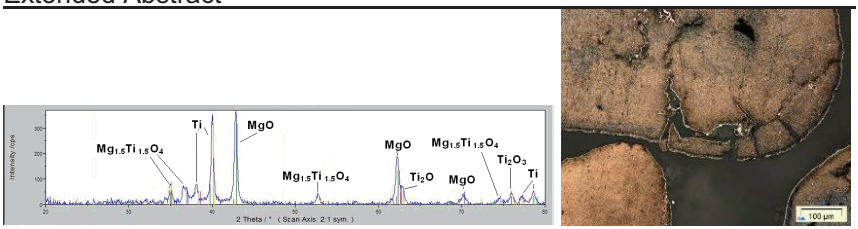

Figure XI: Metallic black strongly reduced product. Optic micrograph. A thin surface layer of titanium metal can be again observed.

Weakly reduced product

This kind of product was obtained together with the strongly reduced product in almost all cases when the reactants were placed in contact with each (reactor I and some configuration of reactors II and III) or as a single product when a nickel blind plug was used on the reactor III. The XRD pattern (as seen in the pattern from test RI-101) shows that titanium and magnesium oxide are the principal phases and the quandilite ($Mg_{1.5}Ti_{1.5}O_4$) and titanium oxide (TiO_2 and Ti_2O_3) phases are in a lower proportion (Figure XII).

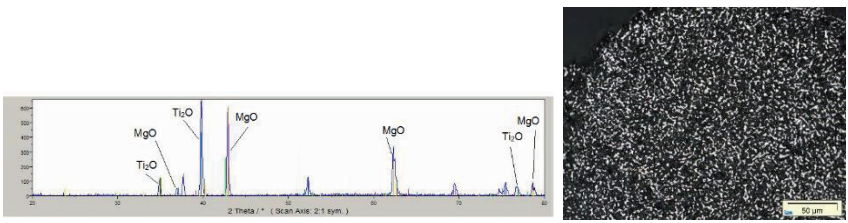

Figure XII: XRD patters of the weak reduced part of product. Optical micrograph of the weakly reduced product. A thin surface layer of titanium metal can be again observed.

Product Distribution on the Reactors

Distribution in Reactor I

When massive magnesium plates were used (size 7 cm diameter, 1 cm wide), five different zones in reactor I were observed (Figure XIII-a). The strongly reduced product (grey colour) was found in the middle of the bed. It looked like a sinter cake (Figure XIII-d). The weakly reduced product (dark material) was seen at the bottom and on the top of the sinter bed in

form of detached particles (Figure XIII-e). A condensated layer of magnesium (Figure XIII-c) was frequently formed on top of the bed. Detached white smaller MgO particles (Figure XIII-b) covered the condensated magnesium coating placed on the surface of the reduced particles as was observed as well. Coloured grains (Ti_2O_3 or TiO) (Figure XIII-f) were rarely seen on the sinter bed. When magnesium cubes (0.5 cm to 1.5 cm) were used, the reaction took place only in preferential zones near to the initial places where the magnesium was localized. TiO_2 placed some centimetres away from this region reacted only to a weakly reduced product and some even remained without any reaction; even though this heterogeneity, in almost all the trials showed, the magnesium was completely evaporated leaving behind a cubic hole.

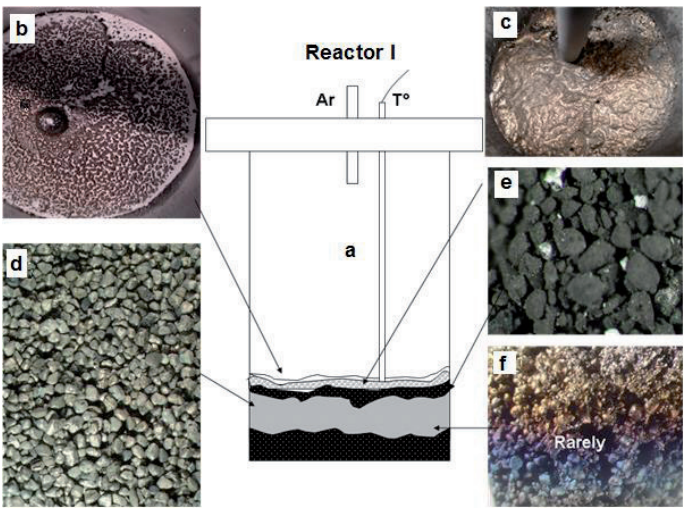

Figure XIII: Product distribution inside the reactor I: a- Schema of the reactor, b-The MgO coating conforms by detachment particles, c-The condensed magnesium, d-The strongly reduced product, e-The strongly reduced product, f-An intermediate reduced product rarely observed.

Distribution in Reactor II

The first experimental series obtained a distribution like the bulk/bubble when TiO_2 particles size >355 were used but a strand fluidized bed resulted when they were used as received size. The second experimental series obtained only a weakly reduced product and MgO particles. Even in some trials obtained particles resulted which were on their surface and

had been reduced but their core did not exhibit reduction since TiO_2 remained.

Distribution in Reactor III

Under configuration 1, the obtained products were a mixture of strongly and weak reduced particles. In configuration 2, a strongly reduced product was always obtained, while configuration 3 only resulted in a weakly reduced product. No difference was observed between the pellet and powder forms of TiO_2. The product distributions in the three different configurations were always the same: particles that had reacted and were found detached from each other; magnesium condensed on the internal walls and on top of the reactor as well as fine white MgO particles detached from one another and homogeneously distributed. Neither sinter products nor MgO coatings were observed, which certainly contrasts with the results found in reactor I.

Impact of Parameter Variation on Magnesiothermic Reduction

Influence of the molar composition ratio φ

The maximum degree of reduction that theoretically could be reached by the magnesiothermic reduction depends on the molar composition ratio (φ) and temperature of the reaction. Temperatures higher than 1400°C allow for re-oxidation of the evolved titanium metal and only titanium suboxides can be obtained. The φ was an influential variable only when reactants were place in contact with each other. When the reactants were placed separately, no influence of φ was observed. The analysis of variance (Anova) for the RI and RII experimental series (annex 11.3.2,11.4.1) shows that the molar composition ratio influences the SRP at fairly low probability rates (44.7% for RI and 51.7% for RII), which implies that the independent effect of this variable on SRP is relatively weak. However, in the case of RIII (see Annex 11.5) the probability that φ influences the produced amount of strongly reduced product (SRP) is 99.4%, which implies a strong independent effect on SRP.

Set temperature and holding reaction time

Set temperature and time for preheating were investigated for every reactor and can be considered as a “soaking time and temperature”. The set temperature was fixed by the experimental plan and achieved by adjusting the furnace temperature. The holding reaction time started when

the furnace achieved the set temperature. Based on the experimental results (annexes 11.3) obtained from RI, RII and RIII and their corresponding statistical calculations, it can be concluded that holding time and set temperature have no influence on the amount of strongly reduced product obtained in those experiments in which the reactants were in contact with each other. The analysis of variance for the experimental series of RI and RII (annex 11.3.2, 11.4.1) showed that temperature influences SRP at a fairly low probability rate (51.1% for RI, 61.7% for RII and 79.8% for RIII), thus implying a relatively weak independent effect of this variable on SRP. In the case of holding time in RII, this effect was 61.7%.

The shape of the magnesium

The form of magnesium (plates, cubes, turnings) becomes important for the degree of reduction only when the reagents have been put into contact with each other. Magnesium was used as cubes, plates and turnings in RI. The analysis of the result of first experimental series for RI and the anova calculation for the second one show that the influence of shape of magnesium over of SRP obtained is 100% (annex 11.3.2). Due to this fact, only plates of magnesium were used on RII and RIII. Magnesium shape determines the duration of the flash gas-solid reaction and the state of the fluidized bed.

Particle size and form of the titanium oxide

The titanium powder was used in different configurations: (1) as received in size, (2) bigger than 200 μm, (3) smaller than 200 μm, (4) bigger than 355 μm and (5) pellets bigger than 1 mm in diameter. TiO_2 particle size only had a strong influence (99.9%) on the obtained SRP when the reagents were in contact with each other; there was no movement and plate shaped magnesium particles were used. In these conditions, particles > 355 μm ensured a higher void volume than smaller ones and the process yielded up to 70% SRP. Provided that magnesiothermic reduction in those trials are dominated by the gas-solid reaction model, and that the void volume has a considerable effect on the behaviour of the bed with regard to the flow of the reactive gas, it follows that the effect of size can be observed and demonstrated statistically. However, in other experimental configurations where pellets or other particle sizes were used, no influence of size on SRP yield was observed.

The Pathway of the Magnesiothermic Reduction

The pathway of the magnesiothermic reduction of titanium dioxide is determined based on experimental observation and XRD analyzes, optic microscopy analysis, SEM (Scan electron microscopy) and EDX (energy dispersive X-ray).

Starting of reaction

The initial reaction temperature was determined in the RI experiments. It was defined when strong temperature increases took place on the bed, as compared to those taking place in the furnace. The initial temperature of the reaction came close to the fusion temperature of magnesium (660 °C). The reaction generally occurred in one single step of huge exothermic energy liberation. Temperature peaks above 1000°C were recorded. Due to the explosive behaviour of the reaction, damage of the protective alumina tube of the thermocouple was common during the experiments. The experimental data agrees with the theoretical simulation of the temperature of the process where the reaction starts at 650°C, reaches high temperature values (1075°C and 1950°C) for molar ratios of φ= 4 and 2.5. Furthermore, the reaction time can be calculated by the duration of the temperature peaks. This reaction time was different for each trial. The maximum and minimum values were approximately 600 and 50 seconds, respectively.

Magnesium partial pressure

As experimental data show reaction starts close to the magnesium melting point; it was calculated in FactSage 6.1; the theoretical magnesium partial pressure process versus the molar composition ratio φ (Figure XIV) at 650°C in isometric and adiabatic conditions. Partial pressure of magnesium greater than 1 bar is achieved if φ is fixed under 3.47. It can be observed at φ =2.5 a pressure of 58 bar, also, if an abrupt chance of pressure exists, it should cause an explosion. Molar composition ratio higher than 3.5 results on values of partial pressure lower than 1.1 bar. At φ = 4 the theoretical partial pressure is 0.72 bar.

When low values of φ = 2.5 are used and the reactants are in contact with each other, a fast and strong exothermic reaction begins and produces an abrupt change of temperature and pressure. The high temperature conduces to reoxidation of the already reduced titanium. The abrupt change of pressure generates small explosions inside the bed that break out of the alumina protection tube of the thermocouple.

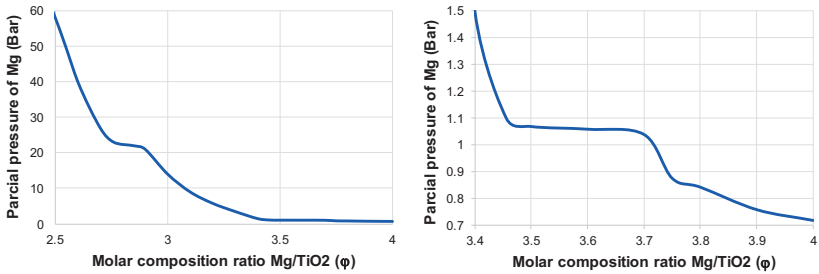

Figure XIV: Theoretical partial pressure of magnesium vs. molar composition ratio at starting temperature of reaction of 650°C with adiabatic conditions. Zoom on left figure.

The generated magnesium vapour at a quick high-pressure flow through the bed is immediately condensed on the top and walls of the reactor due to the high temperature gradient between the gas (>1100°C) and the furnace (650 to 700°C). The gas-solid reaction has occurred in a very short time and avoids a complete reduction of the TiO_2 particle. For those experiments an engulfed titanium coating like melted form was observed, suggesting higher temperature than 1668°C on the surface.

When high values of φ = 4 are used, the theoretical partial pressure barely reaches 0.7 bar in comparison to the low φ, but it is enough to allow a relatively slow gas-solid reaction. Since the gradient of pressure is low, the slow vapour flow can diffuse within the TiO_2 particle with the consequent reduction up to its core. Eventually, the magnesium is condensated on the top and wall of the reactor, but a large amount of SRP is left behind. Those precedent explanations have been experimentally determined from the amount of SRP, the qualitative observations, the analysis of products and their distribution, and they can be applied to the RI and RII configuration. RIII (a multifunctional one) was used in two configurations: either magnesium vapour reacts slowly with TiO_2, or an amount of accumulated magnesium vapour at 1030°C is pressurized up to 0.5 bar approximately and then reacts. In the first configuration - wherein magnesium vapour flows freely to the TiO_2 compartment - the partial pressure depends on the furnace temperature. It increases slowly from 0 to a maximum of 0.5 bar, thus avoiding a strong exothermic reaction; the re-oxidation of the already reduced titanium or an abrupt pressure and temperature change. The result is the complete reduction of TiO_2 to SRP. In the second configuration, wherein magnesium vapour is stored and then allowed to react, the reaction starts at a high temperature that is maintained along the process. Consequently, all the titanium metal

is re-oxidized. The key to a high SRP yield is a relatively slow gas-solid reaction model accompanied by bed movement. In order to obtain the former condition, a slow increase in magnesium partial pressure from 0 to 0.5 bar must be affected.

The Thermochemical Staircase of the Magnesiothermic Reduction

The steps of reduction are proposed using the analysis of the theoretical and experimental results. In such the pathway can be divided into two steps reached during the reaction but their favourability depends on other factors such as the partial pressure of magnesium and the temperature achieved. The successive formation of the product may be described by the following sequences of reaction based on both the theoretical calculations and the products obtained from the experiments.

Table I: Reaction sequences during the magnesiothermic reduction. Stage I. Reduction of TiO_2 to Ti_2O_3 and Mg_2TiO_4. Stage 2: Reduction from Mg_2TiO_4 over TiO to $Ti[O]_\delta$.

Stage	Step	Reaction			ΔG (KJ)
I	9	$5TiO_2 + Mg$	=	$Ti_4O_7 + MgTiO_3$	-258.2
	8	$4Ti_4O_7 + Mg$	=	$5Ti_3O_5 + MgTiO_3$	-211.3
	7	$Ti_3O_5 + Mg$	=	$Ti_2O_3 + MgTiO_3$	-247.8
	6	$1.5\ Ti_2O_3 + Mg$	=	$2.5TiO + ½\ Mg_2TiO_4$	-247.7
	5	$1.5\ Ti_2O_3 + Mg$	=	$2.5\ Mg_2TiO_4$	-152.5
	4	$MgTiO_3 + MgO$	=	Mg_2TiO_4	-315.2
	3	$1.5\ Ti_2O_3 + MgO$	=	$2.5Mg_2TiO_4$	-255.2
II	2	$Mg_2TiO_4 + Mg$	=	$Ti_xO + 3MgO$	-180.8
	1	$TiO + Mg$	=	$Ti[O]_\delta + MgO$	-56.0

* $Ti[O]_\delta$ is the solid solution of metallic titanium with traces of dissolved oxygen.

Stage I: Reduction of TiO_2 to Ti_2O_3 and Mg_2TiO_4

In the first stage of reduction, titanium dioxide is reduced through many intermediary reactions resulting in Ti_2O_3 as well as the magnesium titanates Mg_2TiO_4. It should be remembered that the reaction of TiO_2 to Ti_4O_7 involves a series of reduction steps of the Magnéli phase and those reactions included are chemically driven. Also, the Gibbs free energy values are very close for each reaction. A kinetic barrier is present on the formation of TiO from Ti_2O_3.

Three products with different degrees of reduction were found in the reactors in the first place, two metallic, strongly reduced products (SRP), differentiated by their colours: grey and black; and in the second place, a black, non-metallic, weakly reduced product (WRP). The XRD analysis only revealed low amounts of Ti_2O_3 and $Mg_{1.5}Ti_{1.5}O$ in the black metallic SRP. In this compound, the absence of oxides such as Ti_3O_5 or those belonging to Magnéli phases confirms that steps 9 to 3 ran easily without any kinetic barrier. However, a kinetic barrier is evident between steps 3 and 2. As to the other products, the XRD pattern suggests that the reaction easily overcame the last step of stage 1.

Stage II: Reduction from Mg_2TiO_4 to $Ti[O]_\delta$

Stage II includes the reduction of Mg_2TiO_4 to TiO and then to the solid solution of oxygen in titanium $Ti[O]_\delta$. The Gibbs free energy decreases strongly in comparison to the reactions of stage I. This indicates a lesser thermochemical favourability. Despite the fact that the structures of Mg_2TiO_4 and TiO are cubic, the transformation requires a complete crystallographic rebuilding as already discussed above, hence, a kinetic barrier is formed. In contrast, the subsequent transformation from TiO to the $Ti[O]_\delta$ crystal does not reveal any kinetic barrier.The XRD pattern of the gray strongly reduced product exhibits high peaks of Ti and MgO phases, together with a small Ti_2O peak. For its part, the black non-metallic product (WRP) exhibits only Ti_2O and MgO. This suggests not only that those products overcame the kinetic barrier between steps 3 and 2, but also the occurrence of an almost complete reduction to titanium metal.

Reactants in Contact with each other and High Molar Ratio

In the case that the reagents are in contact with each other, when the reactor temperature exceeds the melting point of magnesium (650°C), the recent melted liquid surface reacts with the TiO_2 particles which are in contact with the metal. The generated heat is used to continue the fusion of magnesium since a part of the magnesium still remains solid because the energy of the latent heat of fusion is not totally supplied. Since more liquid magnesium is now available, the subsequent reaction with the unreacted TiO_2 particles, above the incipient bath, can be kept evolving strongly reduced product and more heat is generated. This cycle increases the temperature rapidly; and a part of the magnesium is now available in vapour form able to react with unreacted particles of TiO_2. It may be noted, that the already reduced particles cannot be reduced thereafter. From this moment, the reaction is not further limited between the liquid magnesium and the solid TiO_2 particle. Thus, the generated

magnesium gas can flow freely toward those particles located nearby. The gas-solid reaction starts generating heat, which is largely consumed in the evaporation/sublimation of the magnesium fraction that still remains liquid or solid. Yet, a small amount of heat increases the temperature of the bed. At this point, a few seconds elapse before the beginning of the reaction. Some seconds pass before the start of the reaction at this point. When the magnesium vapour reaches the surface of the TiO_2 particle in a gas-solid reaction model (Figure XV-a), it reacts immediately to form both MgO and Ti metal. Stage II takes place on the surface of the particle. Some MgO is released from the surface of the particle producing a porous surface that permits an easy flow of magnesium vapor into the particle (Figure XV-b).

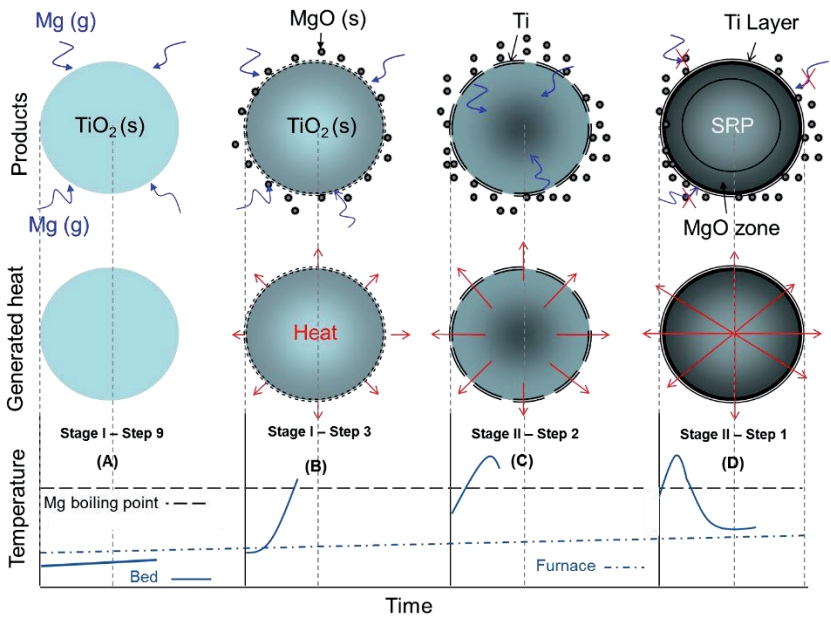

Figure XV: Schematic of the mechanism for the morphology obtained during the reduction of strongly reduced particle when the reagents are in contact with each other.

Magnesium diffuses inside the whole particle and reacts to form Ti and MgO and the generated heat increases the temperature rapidly inside the particle (Figure XV-c). State II is achieved partially and the product of step 2 and 1 can be observed. The generated heat flow outside the particle in a radial direction from core to surface promotes an outward diffusion of the titanium which evolves a superficial coating. This thin film engulfs

the particle and hinders the free flow of magnesium gas avoiding a subsequent reduction in the core (Figure XV-d). Due to the diffusion phenomena, a middle zone without titanium is generated and a black MgO phase is differentiated (Figure XV-c). In the core of the particle Ti, Ti_2O, MgO and Mg metal results. A grey product of high degree of reduction is evolved. However, as magnesium partial pressure is different on the bed caused by the flash high exothermal magnesiothermic reaction, in some places it does not produce enough magnesium vapour to complete the total reduction and the kinetic barrier appears. A bit of products of the stage I ($Mg_{1.5}Ti_{1.5}O_4$, Ti_2O_3) and products of stage II (Ti, MgO) can be found on the black metallic reduced product.

Reactants in Contact with each other and Low Molar Ratio

The reaction runs in the same way until finishing the total reduction steps, but due to the low amount of magnesium, this element is quickly evaporated/sublimated. The huge amount of remaining heat exclusively increases the temperature of the bed, which causes the re-oxidation of the obtained SRP to WRP. The final products are Ti_2O and MgO. Neither metallic titanium nor titanium oxides are present.

Reactants Separate each other

In those configurations in which the reactants were separated, three important alternative results were observed: the reaction did not take place; it reached its first stage, or it completed the sequence. In those two cases, featured by bed movement (RIII) and free magnesium vapour flow, the reaction sequence was completed and the obtained product was 100% SRP. As the amount of available magnesium vapour was gradually increased depending on the temperature rise in the furnace, the exothermal magnesiothermic reaction took place quietly and the low amount of generated heat was lost through the reactor's walls, thus maintaining a low temperature in the bed. This prevents the re-oxidation of the already obtained titanium metal. When the furnace reached a high temperature (1100°C), no additional reduction or oxidation occurred. Finally, bed movement guaranteed the homogeneity of the obtained products, the detachment of the MgO microparticles, and the formation of a sinter bed. A dispersion fluidized bed state was obtained during the reduction process. In addition, when the nickel plug is used to isolate the compartment where TiO_2 finally reacts with magnesium, said reaction only happens after the magnesium vapour reacts with the nickel plug and melts forming an alloy at approximately 1030°C. Then, the magnesium vapour at a partial pressure > 0.5 bar flows into the TiO_2 compartment and reacts. Since the

furnace is at 1030°C and there is enough vapour to react with TiO_2 through a flash exothermic reaction, the heat generated by reduction reaction increases the bed temperature, which allows reduction and subsequent re-oxidation. The total reaction sequence is completed, but it is immediately followed by titanium re-oxidation. Thus, the sequence is reversed to step 2, so only homogenous Ti_2O and MgO are obtained as black metallic product (WRP).

Leaching of the Magnesiothermic Reduction Products

The aim of this experimental part was the selection of a solution which achieved the highest efficiency for the removal of magnesium, magnesium oxide and magnesium titanates and at the same time the minimal oxidation of titanium. The efficiencies of dissolved metals for the SRP is showed in Table II. The trials carried out with 6M HCl (0s24, 0s24h) were not analysed because of high dissolution of the raw material.

Table II: Percentages of elements dissolved from the strongly reduced product by the different acid solutions.

Experiment No.	Acid	%Mg	%Ti	%Fe	%Ni
1s1	3M HCl	94.04	0.04	13.57	14.65
1s24		94.04	0.41	22.86	17.39
2s1	0.55M HCl	94.04	0.05	14.29	13.73
2s24		97.40	0.04	14.29	13.73
3s1	8 HCl% + 3 HNO_3%	92.36	0.05	10.71	16.02
3s24		100.00	0.03	25.00	18.31

In almost all cases, the magnesium content was almost completely removed in the final product as shown in Table II and Figure XVI. The dissolution of magnesium was higher than 92%, with a maximal efficiency for the sample No. 3s24. It may be that at the high HCl concentration the time does not influence the dissolution percentage. This behaviour could be the result of a surface passivity that inhibits any further dissolution. For these trials, some particles remained without any reaction. Other trials (2s, 3s) exhibited an obvious behaviour; the longer the time for reaction the higher the dissolution of magnesium. No passivity was developed with the additional presence of the stronger oxidant agent (HNO_3). The acid mixture 8 HCl% + 3 HNO_3% resulted in being the best leaching efficiency. The amount of dissolved titanium (Figure XVI) was about 0.04% except for using 3M HCl. The lowest titanium dissolution (0.03%) was obtained using the acid mixture (8 HCl% + 3 HNO_3%) for 24 hours.

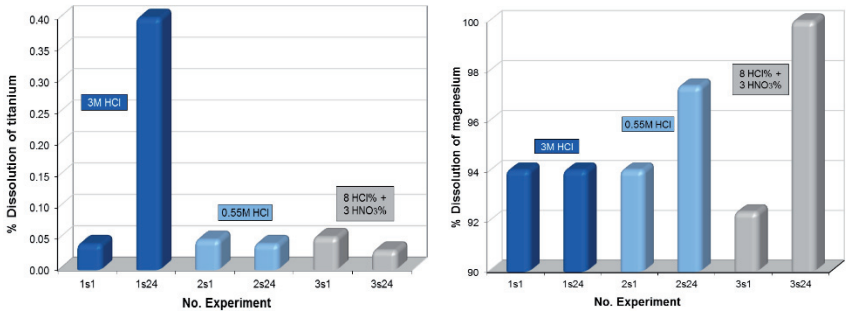

Figure XVI: Dissolution percentage of Ti sub-oxide and Mg on trials using strongly reduced product as raw material.

The Obtained Powder

The strongly reduced product SRP (from RI-131, RII-72, RIII-41, RIII-51 and RIII-61) were leached (8 HCl% + 3 HNO_3%), dried at 150°C for 4 hours in an argon atmosphere and analysed by SEM and EDX. The EDX chemical analyzes show that the oxygen content in the strongly reduced particles exhibit a share from 2.9 wt% to 7.46 wt% with an average of 4.23 wt% and, additionally, that the other metals were completely leached. Chloride was not found on the powder. The powders exhibit different morphologies, such as equiaxed as well as spherical particles and their size is on the order of the nanometres. In order to obtain a quantitative value of the degree of reduction from TiO_2 to Ti in the obtained products, the amount of oxygen was fixed as the reference parameter. Provided that TiO_2 contains 40.03 wt% oxygen while grade 1 commercial titanium contains 0.18 wt% oxygen, it was established that a degree of reduction of 0% corresponded to 40.03 wt% oxygen. Correspondingly, a 100% degree of reduction was assigned 0.18 wt% oxygen. Table III shows the degree of reduction estimated for the products of the present investigation based on their usual amount of oxygen.

Table III. Quantitative value of degree of reduction.

Wt% Oxygen	Degree of reduction
40.03	0.0
33.36	16.3
11.20	71.9
4.30	89.2
0.18	99.5

Morphology of powder from RI (Argon Protective Reactor)

At lower temperatures, such as 850°C and short times of 30 minutes (RI-131) titanium metal was formed with a high content of oxygen (about of 12.7 ± 3 wt%; corresponding to a reduction degree of 68.58%). The titanium particles (Figure XVII) exhibit a distribution size from 0.1 μm to 1.4 μm.

Their general shape is semi-spherical but some of the bigger ones exhibit an angular morphology. Porosity produced by nucleation and releasing of MgO could only be observed on the bigger particles. The size and quantity of small particles suggest a quick transformation to the TiO_2 to Ti metal, which agrees with the pathway proposed and the chemically driven consideration.

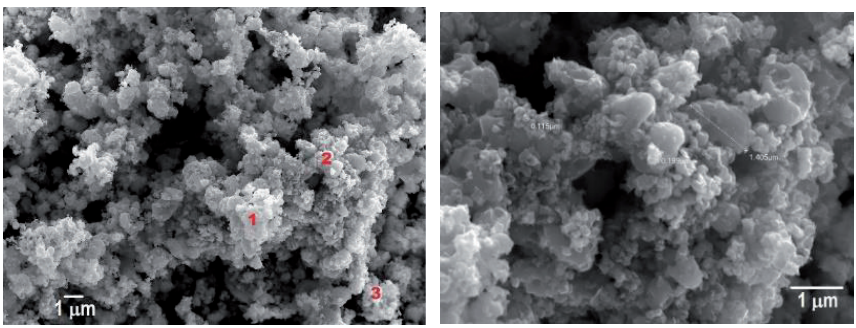

Figure XVII: SEM of the powder obtained from the grey strongly reduced product RI-131. Very small particles are observed (Dm ≅ 0.1 to 1.4 μm).

The EDX shows that the oxygen content is approximately 12.7 wt%, leading to a degree of reduction of 68.58% (Table IV).

Table IV: EDX chemical composition of powder obtained from the strongly reduced product from RI-131.

Point	%Ti	%O
1	84.18	15.82
2	89.69	10.31
3	87.94	12.09

Morphology of powder from RII (Sealed Reactor)

The titanium particles of the SRP (Figure XVIII) exhibits a distribution size from 0.28 μm to 0.96 μm. Their shape is similar to RI-131 but the semi-spherical shape is more abundant than the angular ones. The EDX (Table V) shows the presence of oxygen and magnesium. The oxygen content is approximately 4.02 wt% (90.36% degree of reduction), with magnesium only on point 2 with 1.98 wt%.

Table V. EDX chemical composition of powder obtained from the strongly reduced product from RII-72.

Point	%Ti	%O	%Mg
1	95.71	4.29	0.00
2	94.96	2.89	1.18
3	95.10	4.90	0.00

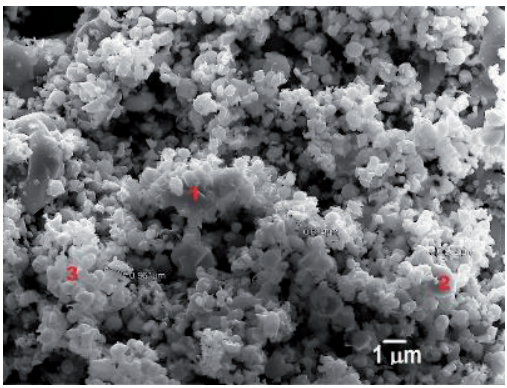

Figure XVIII: SEM of the powder obtained from the grey strongly product RII-72. Small particles Dm ≅ 0.28 to 0.96 μm.

Morphology of powder from RIII (Two Compartment Reactor)

Three different morphologies were observed in the SRP obtained using Reactor III, depending on variations in the processes, as described in the following:

Equiaxed particles: The particles from trials in which the reagents were in contact with each other (RIII-41) were obtained under the following conditions: set time was for 4 hours, molar ratio φ = 4, and set temperature was 1100°C. These particles exhibited an equiaxed form with holes

on their surface (Figure XIX). Particle size ranges from 0.5 μm to 3.5 μm. The SEM micrograph renders a facetted growth of the titanium particle from the prior magnesium titanates particle. The prior ones are decomposed on both MgO and titanium particles. The MgO particles are released leaving behind a high porosity of octahedral holes on the surface, which is then transformed into titanium metal by the removal of magnesium and oxygen. This micrograph shows larger particles than the other sample; it could be that the smaller particles have been adsorbed by the bigger ones in a ripening process promoted by the high temperature and longer time. The titanium particle shapes are semi-spherical.

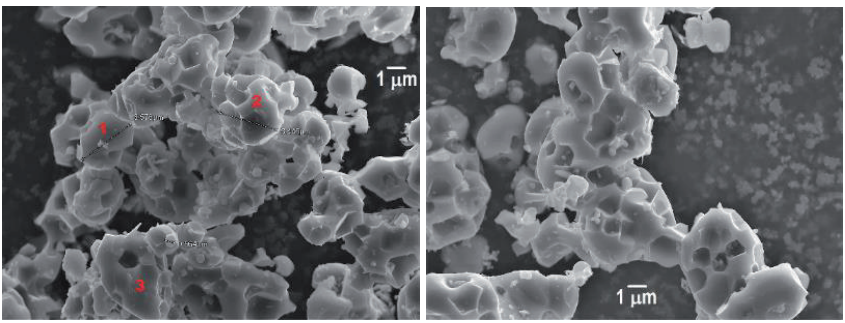

Figure XIX: SEM of the powder obtained from the grey SRP RIII-41. Left- The bigger particles size app. 3.5 μm and the smaller ones 0.5 μm. Right - Octahedral holes on the particle surface originate from released MgO particles.

The EDX (Table VI) shows the presence of oxygen and magnesium. The oxygen content is approximately 4.38 wt% (89.46% degree of reduction), and magnesium is only on point 1 with 2.79 wt%.

Table VI: EDX chemical composition of powder obtained from the strongly reduced product from RIII-41.

Point	%Ti	%O	%Mg
1	93.01	4.2	2.79
2	39.99	6.01	0.00
3	95.71	4.29	0.00

Spherical and semi-spherical particles: Two different morphologies (Figure XX) were observed in strongly reduced products obtained under the same conditions: reagents separated from each other, 4 hours set time, molar ratio of 4 (φ = 4) and set temperature of 1100°C. The first one of

these morphologies corresponded to spherical and semi-spherical titanium particles with a 0.53 μm to 1.93 μm size (RIII-51). They were detached from the continuous matrix structure under a “free flow” behaviour mode. Besides those two morphologies, an angular monolithic material was observed, containing an elevated amount of nickel (circa 52 wt%) that suggests chemical reactions between some of the reactants and the nickel contained in the high temperature resistant steel alloy of the reactor´s wall. The EDX (Table VII) shows that the oxygen content is approximately 3.25 wt%, leading to a degree of reduction of 92.29%.

Table VII: EDX chemical composition of powder obtained from the strongly reduced product from RIII-51.

Point	%Ti	%O	%Ni
1	86.76	5.46	7.76
2	96.63	3.37	0.00
3	43.66	3.48	52.86
4	44.34	2.90	52.76

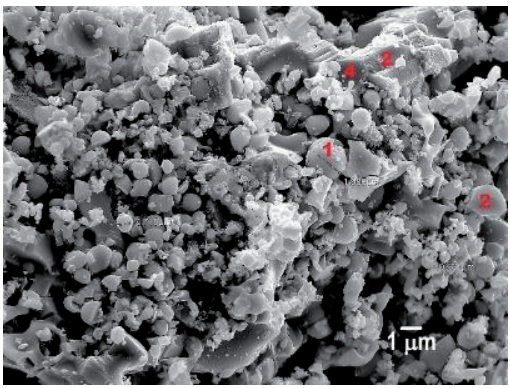

Figure XX: SEM of the powder obtained from the grey SRP from RIII-51. Left- The bigger particles size appr. 3.5 μm and the smaller ones 0.5 μm. Right – Octahedral holes on the particle surface from released MgO.

Continuous matrix structure:

The second morphology corresponds to a continuous titanium matrix spotted by traces of small, detached titanium particles (Figure XXI), that had been absorbed by the matrix. Small cavities on its surface, left by leached MgO were observed as well. This confirms the formation of a

continuous matrix resulting from facetted growth by a sinter/ripening process. The EDX shows that the oxygen content is approximately 5.22 wt%, leading to a degree of reduction of 87.35%.

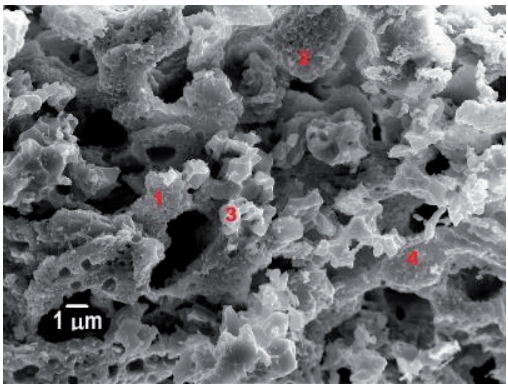

Figure XXI: SEM of the gray metallic SRP from RIII-61. A network of product and fine particles are observed. High porosity is observed on the surface of the network.

Table VIII. EDX chemical composition of powder obtained from the strongly reduced product from RIII-61.

Point	%Ti	%O
1	96.51	3.49
2	97.01	2.98
3	94.78	5.22
4	92.54	7.46