

EXPERIENCE AND RESULTS FROM RUNNING OF A 1 KG TI SCALE KROLL REACTOR

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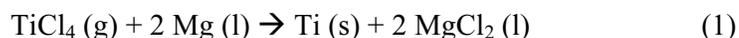
Abstract

Ti metal is conventionally produced by magnesiothermic reduction of titanium tetrachloride (TiCl₄) in the Kroll process, as well as by sodium reduction of titanium tetrachloride in the Hunter process. In order to develop a skills and knowledge base in the production of titanium metal in South Africa, Mintek has built a laboratory-scale testing facility capable of producing up to 1 kg Ti sponge per batch by metallothermic using either magnesium, calcium or sodium molten metals. The present paper gives the results of the operation of the above Kroll-type reactor in various experiments of the magnesiothermic reduction of TiCl₄.

Introduction

The Kroll process [1] is extensively used in the production of titanium metal. It is a batch process that involves the production of titanium sponge by the reduction of purified TiCl₄ with molten magnesium in a sealed reactor. Purified TiCl₄ is produced by chlorination of titania feedstock to produce raw TiCl₄ that is further purified by distillation to remove other accompanying metal chloride impurities.

The main reaction in the Kroll process for the production of titanium sponge in a sealed retort under inert gas atmosphere (of helium or argon) at about 900°C is summarised in Equation 1:



Either solid magnesium is melted in the retort, or liquid Mg is used, followed by controlled introduction of TiCl₄. Molten MgCl₂ by-product produced by the reaction is periodically tapped from the retort during the operation.

The refining and transformation of the titanium sponge into finished products is an extensive process. The sponge manufactured by the Kroll chloride process generally has titanium content in the range between 99.2 and 99.8%. Some lower grades such as Toho Titanium Grade B specify a minimum of 97% Ti. The impurities in the sponge are removed by either helium gas sweep followed by simple acid leaching or by vacuum distillation. This is followed by the comminution of the sponge mass by a series of boring, shearing, crushing and screening steps. The titanium sponge product is further melt-refined to produce Ti ingots and slabs. Improvements to the Kroll process, coupled with better melting techniques that have made the quality of the sponge less critical, rendered the Kroll sponge suitable for aerospace applications.

Wilhelm Kroll first produced titanium through the calciothermic reduction of TiCl_4 , as described in Equation 2 below:



He then switched to magnesium as a reductant when he found it to be more efficient to reduce impurities in the titanium metal.

Each of the reductants used by Kroll has their own advantages and disadvantages related to their physical and chemical properties. Solid magnesium is easier to handle as it is not reactive with air like calcium. At a reactor operating temperature of 900 °C, calcium has the lowest vapour pressure, as seen in Figure 1, and therefore the lowest risk of loss of containment. CaCl_2 as opposed to MgCl_2 has the highest solubility in water, leading to easier separation of products.

Table 1 -Physical data of products and reactants, according to Perry [14]

Property	Ti	Mg	Ca	TiCl_4	MgCl_2	CaCl_2
Melting point, °C	1660	651	810-851	-23	712	772
Density, g/cm ³	4.5	1.74	1.55	1.726	2.325	2.152
Boiling point, °C	-	1107	1487	136	1418	>1600
Solubility in water, g/100 g water	-	-	-	-	54.5	74.5

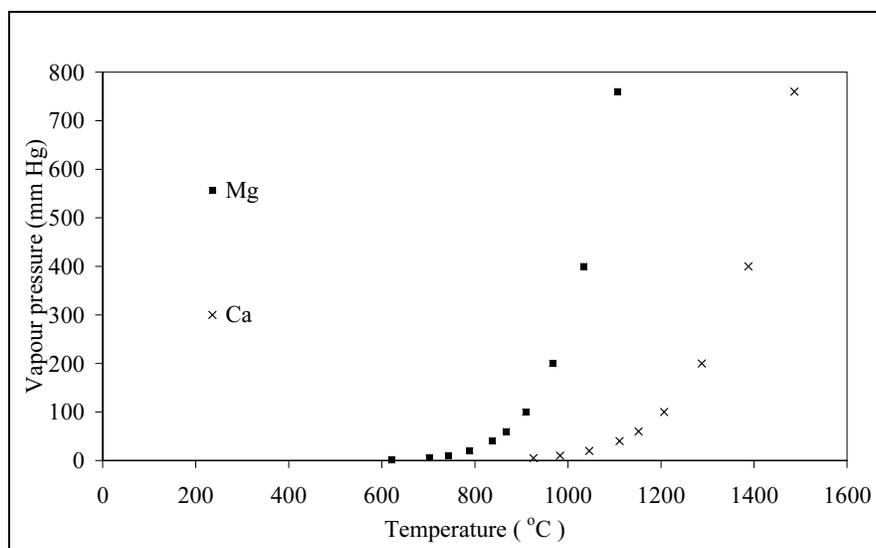


Figure 1- Vapour pressures of magnesium and calcium at varying temperatures, according to Perry [14]

Although research is being conducted into processes that will be able to use titanium oxides as feed to producing titanium metal [2, 3, 4], titanium tetrachloride (TiCl_4) is still the primary feedstock for the production of titanium sponge [5, 6]. The purification of TiCl_4 is an easy, efficient and established process. Because of the high reactivity of

Ti metal, high purity TiCl_4 is required for the production of pure Ti metal. It is easier to separate FeCl_3 from TiCl_4 in the liquid state by distillation than FeO_x from TiO_2 in the solid state. Most of the by-products of the Kroll process are salts that can be removed by leaching in water, vacuum distillation or inert gas sweeps. They can also be separated through electrolysis into reagents (metal and Cl_2) and recycled.

Ongoing research is being conducted to develop a continuous production of Ti metal by improving the Kroll process, by modifying various processes including the electrolytic processes [6, 7, 8, 9, 10, 11].

More recently Suzuki and Naito [13] studied the calciothermic reduction of TiCl_4 during the electrolysis of a CaCl_2 melt. The aim was to improve on the batch nature of the Kroll process by simultaneously producing Ca (dissolved in the CaCl_2 melt) through electrolysis and reacting this Ca with gaseous TiCl_4 at 900 °C.

Because of the importance of titanium in the future (Ti being a strategic metal), Mintek is involved in the Ti programme to develop skills and knowledge required by this industry in South Africa. The present paper summarises the results of the reduction of TiCl_4 to produce titanium metal in a 1 kg Kroll laboratory-scale reactor at Mintek.

Mintek's Laboratory-scale Kroll reactor

The Mintek's experimental set-up of the Kroll process is sketched in Figure 2. It consists of a stainless steel bottom-sealed cylindrical crucible. The open top of the crucible is sealed with a graphite gasket to the reactor lid. The stainless steel crucible is placed in a cylindrical resistance heating furnace where it is surrounded by heating elements cast into the alumina refractory. The space between the refractory and crucible can be used to blow cold air to cool down the reactor during the operation if required.

The nitrogen cooled TiCl_4 feed pipe, the reactor thermocouple, the argon inlet and the reactor outlet are all connected through the reactor lid.

The TiCl_4 is fed to the reactor directly from a glass bottle suspended on load cells. A special bottle cap was designed that seals and connects the bottle to the reactor feeding pipe and the argon gas pipe and pressure regulator. The reactor TiCl_4 feeding pipe is fitted with a valve that regulates the TiCl_4 feed rate to the reactor.

To ensure flow of TiCl_4 into the reactor, an argon purge is also provided into the TiCl_4 bottle. The pressure inside the TiCl_4 bottle is controlled by a pressure regulator. The TiCl_4 feed rate is manually controlled by a valve and the pressure in the TiCl_4 bottle. As the reaction between TiCl_4 and magnesium is highly exothermic, the reactor temperature is constantly monitored and the TiCl_4 feed rate is adjusted accordingly.

The outlet gas products are extracted and neutralised in a caustic soda scrubber.

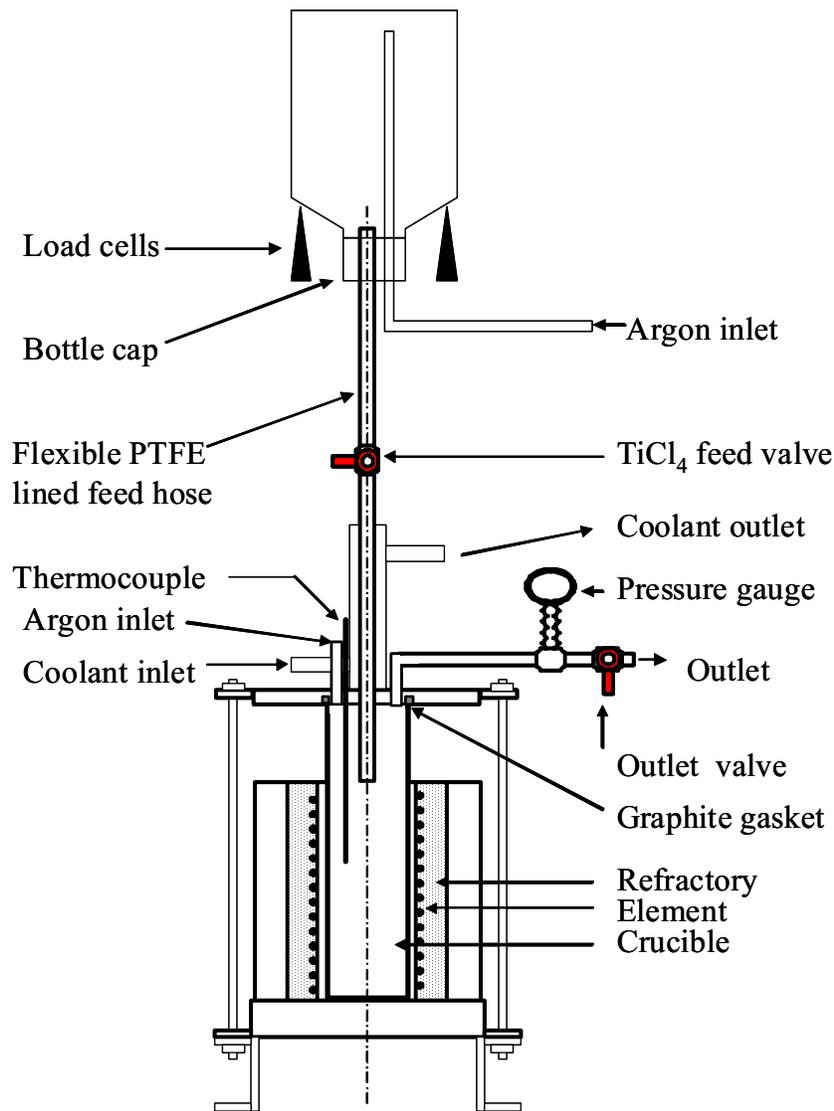


Figure 2- Sketch of experimental set-up

Operation of the reactor

A summary of the experimental conditions of the tests carried using the 1kg batch Kroll-type reactor is given in Table 2 below.

Table 2- Experimental conditions

Experiment	Reactor Feed Temperature	Reductant	% of stoichiometric TiCl ₄ requirement fed
1	750	0.50 kg Mg	100
2	850	0.50 kg Mg	100
3	850	0.50 kg Mg	100
4	900	0.86 kg Ca	100

Prior to the operation of the reactor, the crucible is charged with the required amount of reducing metal (magnesium or calcium). The lid is then bolted on the crucible and thereafter the TiCl₄ feed bottle is connected. The reactor is then tested for leaks by pressurising the crucible to 100 kPa with argon gas; the test is passed when the reactor is able to maintain the pressure for a duration of 10 minutes. The reactor is then heated at a rate of 200 °C per hour up to the set operating temperature (reactor feed temperature) which temperature is maintained for the duration of the test. During the heating period, the reactor pressure is maintained at +10 kPa (gauge) with a flow of argon gas to prevent air ingress.

Once the operating temperature is reached, the outlet valve is closed and the argon feed shut off before starting the feeding of TiCl₄. A feed rate of 0.5 kg/h TiCl₄ (~62kg TiCl₄/h.m²) was targeted for all the experiments, thus a total of 4 hour feed duration. During the operation, the reactor pressure is monitored and maintained below 40 kPa (gauge) by intermittently opening (venting) the reactor outlet valve. During the feed period, as the reactor is cooled by natural convection, the operating temperature is controlled by the extent of feed rate of the TiCl₄. In case of a temperature surge, the reactor is left to cool down naturally to the target temperature before carrying on with the feed.

Once the required amount of TiCl₄ has been fed to the reactor, the TiCl₄ feed valve is closed and the reactor is maintained at the set temperature for 30 minutes to ensure that all TiCl₄ has reacted. The set temperature is then lowered in steps of 150 °C, ensuring that the reactor is sealed at each step. Cooling of the reactor can also be improved by blowing pressurized air into the jacket around the reactor refractory. Once the reactor reaches 40 °C, the elements are switched off and the reactor is left to cool overnight before the removal of products.

The final products are separated by visual inspection to remove unreacted materials after which the separated products are submitted to the process steps as presented in Figure 3.

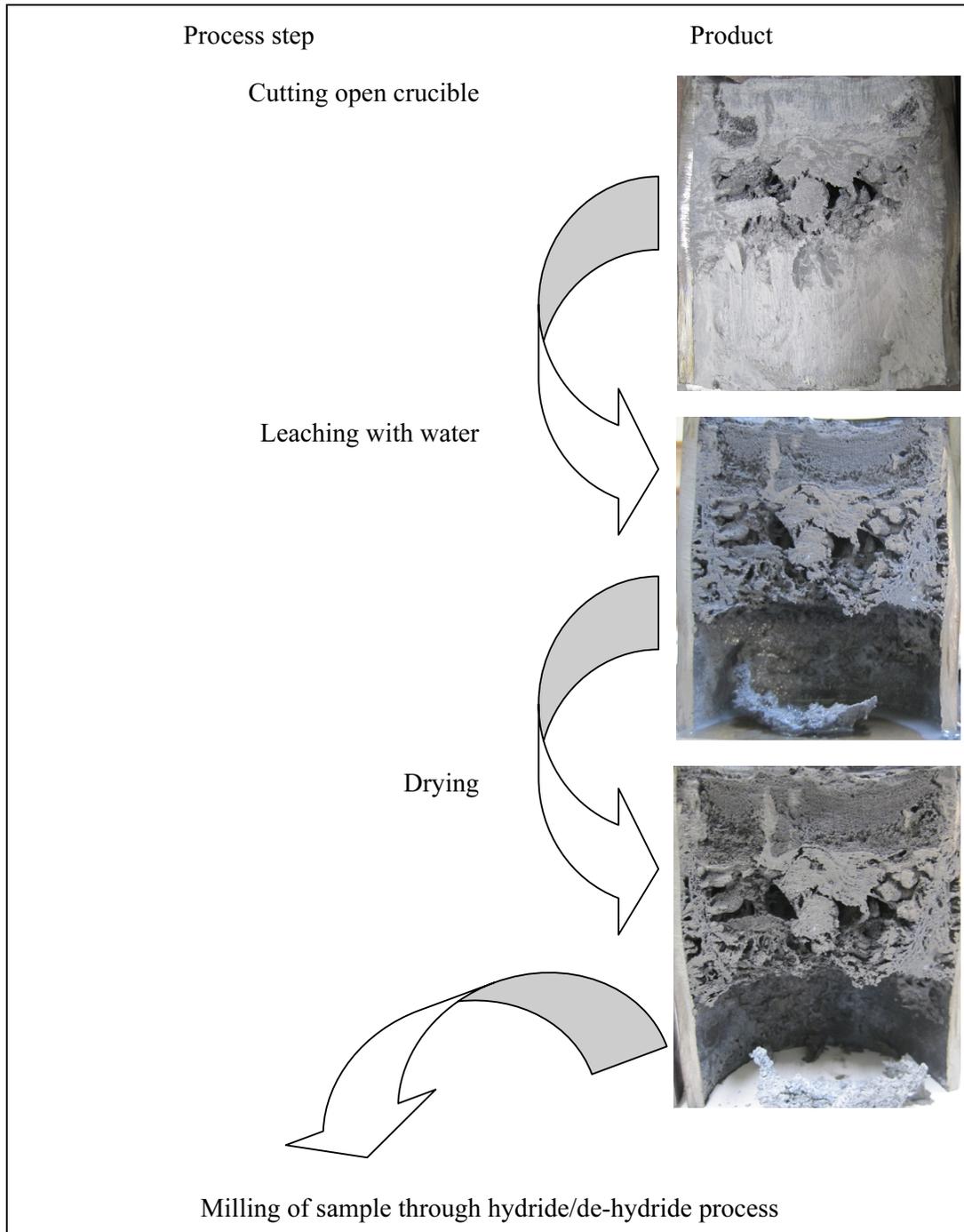


Figure 3- Processing route for reduction products, images from Experiment 3

The samples of Ti sponge for chemical analysis were prepared using the hydrogenation and dehydrogenation process (HDH). The sponge samples were hydrogenated, milled and de-hydrogenated.

Experimental results

1.1 TiCl₄ flow control and Temperatures during the operation

The TiCl₄ feed flowrate depends on the hydrostatic pressure (height), argon pressure in the bottle, pressure inside of the reactor and the extent of the valve opening. In general during the operation, the TiCl₄ feedrate was manually regulated with the valve opening. During Experiments 1 and 2, a needle valve was used. This valve had a high resistance to flow and it was needed to pressurise the TiCl₄ feed bottle with argon gas to achieve the flow required by the experiment. After Experiment 2 the needle valve was replaced with a ball valve. The latter was found to have a much lower resistance and the flow was established without any need for pressuring the TiCl₄ feed bottle.

The masses of TiCl₄ fed over time are given in Figure 4. Besides Experiments 1 and 2, there was an acceptable control of the TiCl₄ feedrate to the reactor. During Experiment 2, the feeding was interrupted by a power cut, but resumed after the reactor was heated to temperature again. As opposed to the target feedrate, the achieved rates were generally faster during the first 1.5 kg of TiCl₄ fed and then slower during the feeding of the last 0.5 kg. This may be due to the decreasing of the hydrostatic pressure (lower levels of TiCl₄ in the feed bottle) as well as the increasing pressure build-ups in the reactor. It is proposed to modify the actual design to achieve a much better control of the TiCl₄ feedrate to the reactor.

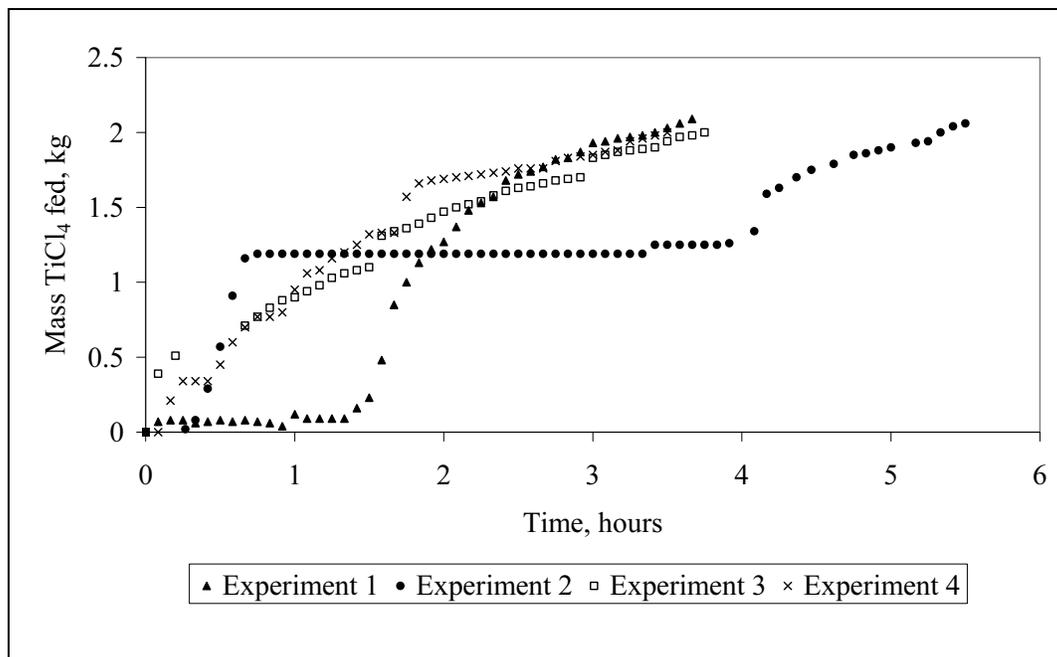


Figure 4- Mass of TiCl₄ fed to reactor for each experiment

The temperature readings inside the reactor during the feeding periods of each experiment are given in Figure 5. In general the control of the temperature around the reading thermocouple was excellent during the experiment; it was achieved by

automatic control (switching on and off) of the heating elements together with controlled TiCl_4 feedrate. The temperature spike observed in Experiment 1 was a result of a relatively higher TiCl_4 feedrate to the reactor.

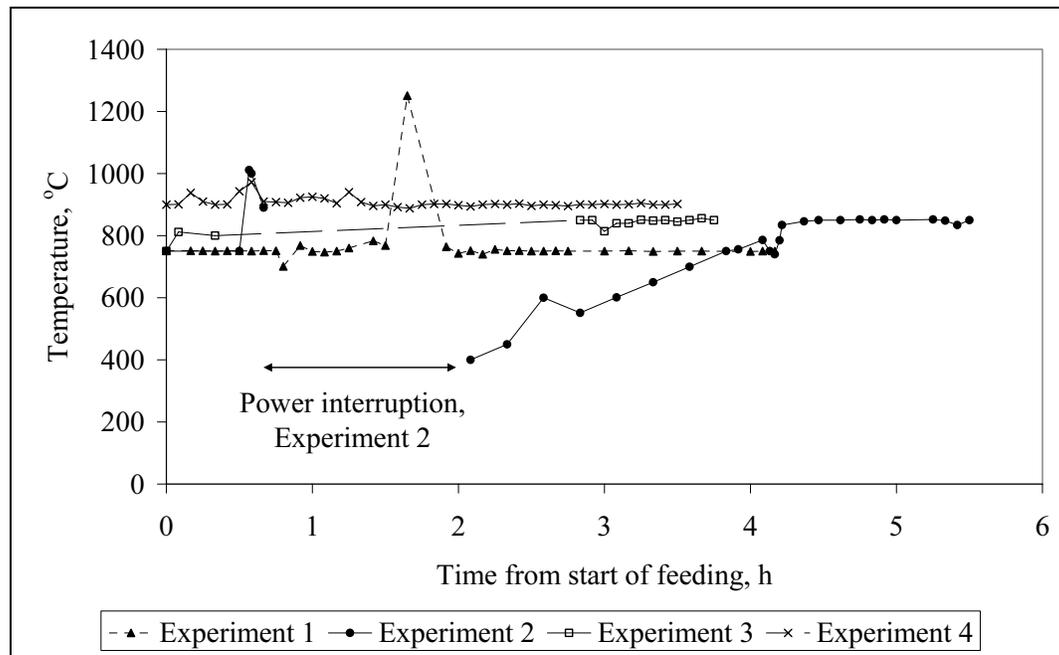


Figure 5- Temperature readings inside reactor from start of heating to end of feeding

The thermocouple is measuring the temperature in the top layer of the melt, principally the temperature in the molten magnesium layer. The temperatures in the other useful sections of the reactor, such as the bottom where Ti metal is supposed to settle and the intermediate level of magnesium chloride, were not measured. Additional measurement and control of temperature in these sections is required since it impacts on the operation of the reactor, conversion of TiCl_4 to Ti and quality of the Ti sponge product. More thermocouples might be required even in this size of operation.

The reactor pressure was monitored and maintained below 40 kPa (gauge) by intermittently opening the reactor outlet valve (venting) when required.

1.2 TiCl_4 grade and conversion to Ti metal

The titanium grades of the sponge products were determined by X-ray diffraction of hydrogenated/dehydrogenated (HDH) sponge samples. These grades were used to calculate the conversion of TiCl_4 to Ti which results are summarised in Table 3.

The Ti content in the sponge was relatively low; this may be explained by the amount of magnesium metal and chloride entrapped in the sponge as well as a possible partial oxidation of the sponge product during the drying and HDH process steps (sample preparation).

The low conversion level in Experiment 1 is explained by the high losses of Ti as TiCl₄ fume bypassing the reactor during the process, as well as Ti fines reporting to filtration solids rather than to the sponge mass following the leaching step. The outlet valve was left opened during this experiment. The problem of TiCl₄ bypassing the reactor was addressed by lengthening the TiCl₄ feed pipe into the reactor to increase the gas retention and contact time in the reactor and also by operating as much as possible with a closed outlet valve.

Table 3- Ti sponge mass recovered and implied conversion of TiCl₄ to Ti

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Leach time, h	72	24	24	24
Ti sponge, g	359	664	569	598
Ti in sponge, wt % (X- ray diffraction)	75	65	73	67
% TiCl ₄ conversion to Ti	51.5	82.4	80.9	80.2

Considering the size of operation, it is believed that the level of TiCl₄ conversion of about 80% is acceptable. It is however necessary to develop an improved method for sampling and preparation of the Ti sponge for analysis that would minimise the oxidation as well as an adequate method for the purification of Ti sponge to remove contamination by magnesium and magnesium chloride.

1.3 Sponge impurities

Standard Ti sponge typically has a Ti content of 99.6%. The aim of the initial experiments was not to produce sponge of equal purity, but rather to develop process knowledge. The following preliminary results of the Ti sponge produced should therefore be seen in this light. The magnesium, calcium, chrome and iron contents were determined by acid digestion and fusion followed by induction coupled plasma analysis. Ni contents were estimated by X-ray diffraction scans. The oxygen, nitrogen and carbon contents were determined by combustion and the sodium and potassium levels by atomic absorption. Ti content of the sponge is normally calculated by difference. Due to uncertainty in the accuracy of Ti grade of the sponge, only the levels of impurities are reported in Table 4.

Table 4- Preliminary analysis of sponge impurities

Experiment	Mg %	Ca %	Cr %	Fe %	Ni ppm	O %	N %	C %	Na ppm	K ppm
1	2.3	0.24	0.13	0.43	574	3.26	0.73	0.18	21	16
2	4.7	0.03	0.14	0.31	455	1.77	0.16	0.13	12	<2
3	9.7	0.03	0.07	0.26	162	0.75	0.12	0.12	6	<2
4	0.4	2.23	0.40	1.68	1920	0.73	0.08	0.17	*	*

* Not Available

Fe, Ni and Cr originate from the steel used for the manufacturing of the crucible. The level of these impurities can be decreased by using a reaction vessel with an inner cladding of carbon steel [15]. Low carbon steel is preferred to minimise the effect of

carbon. These impurities were higher in the sample produced by calcium reduction than in the samples produced by magnesium reduction.

The magnesium content of the alloys can be improved by vacuum distillation of Mg and MgCl rather than by the leaching process. The oxygen and nitrogen contents in the sponge were reduced by minimising the air ingress to the reactor; sealing of the reactor is very important even in the cooling stage of the reactor. Sample preparation also plays a significant role such as drying at lower temperatures in evacuated desiccators and the strict observance of HDH process procedures. This was carried out during Experiment 2 and 3.

1.4 Sponge morphology

The reactor crucibles containing the sponge and salt products were cut using a grinder and a metal handsaw first along the vertical axis and then along the horizontal just above the crucible bottom and above the product level. This resulted in crucible halves from which the product distribution was observed (Figure 6).

The observations of the sections showed that during magnesium reduction, the Ti sponge appeared to form first on the sides of the crucible in line with the surface of liquid magnesium. The growth of the sponge then proceeded to the centre of the crucible and upwards with the rising magnesium level. The initial (lower) structure of the sponge appeared coarse and clear dendritic growth patterns were visible. The top (later) structure of the sponge appeared finer, more granular. The initial structure may in part be due to faster reaction rates (because of faster feeding of $TiCl_4$) at the beginning of the experiments leading to higher localised temperatures and faster agglomeration of Ti metal. Another possible explanation is the possible segregation of Ti grains during the settling process leading to particles to be distributed according to their sizes (fine particles sitting on the top of coarser particles). Some Ti particles did not form part of the sponge mass and settled in the bottom of the crucible.

The sponge structure produced by calcium reduction did not differ significantly from that produced by magnesium reduction and the influence of the reducing metal on the sponge morphology was not clear. More investigations might be required here.

Scanning electron microscopy (SEM) was employed to investigate the different phases present in the samples taken from the sponge masses. The Zeiss Evo MA 15 scanning electron microscope with Bruker EDS detector was employed. The samples were investigated in backscattered electron mode concentrating on the Ti-bearing phases present.

The samples for SEM were prepared by washing them in water and then acetone to remove soluble phases that could inhibit the epoxy resin from setting, thereafter they were vacuum impregnated and kept in a desiccator to prevent oxidation.



Figure 6- Sponge structure after leaching with water but before drying, Experiment 3

The SEM images from the sample taken from the top part of the sponge mass of Experiment 1 presented in Figure 7 and 8, show the titanium metal phase in various grain sizes as well as some partially reduced TiCl_4 and MgCl_2 not removed by leaching.

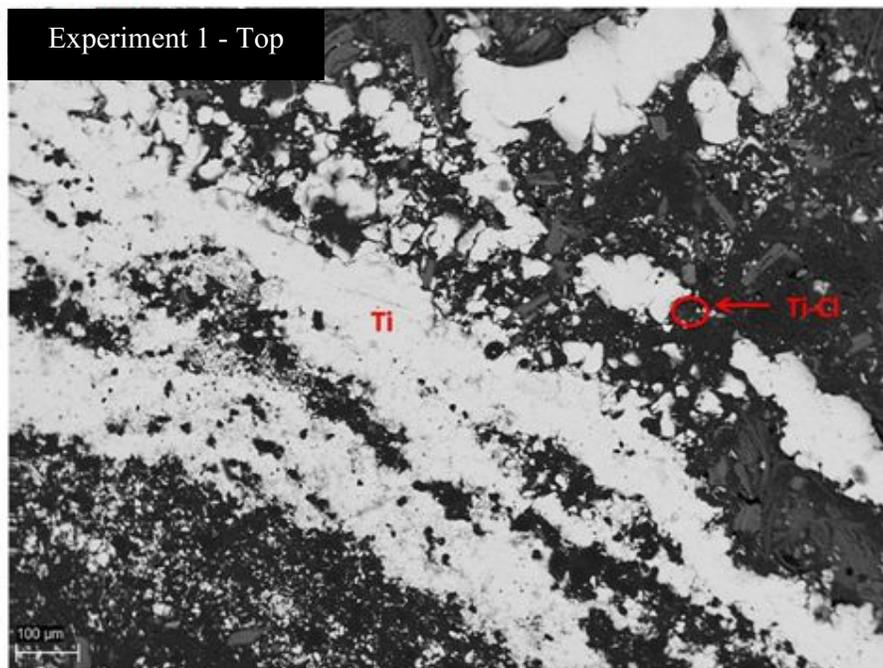


Figure 7- Backscattered electron image illustrating Ti-metal as well as some remnant feed in the top part of Experiment 1. The scale bar represents 100 μm.

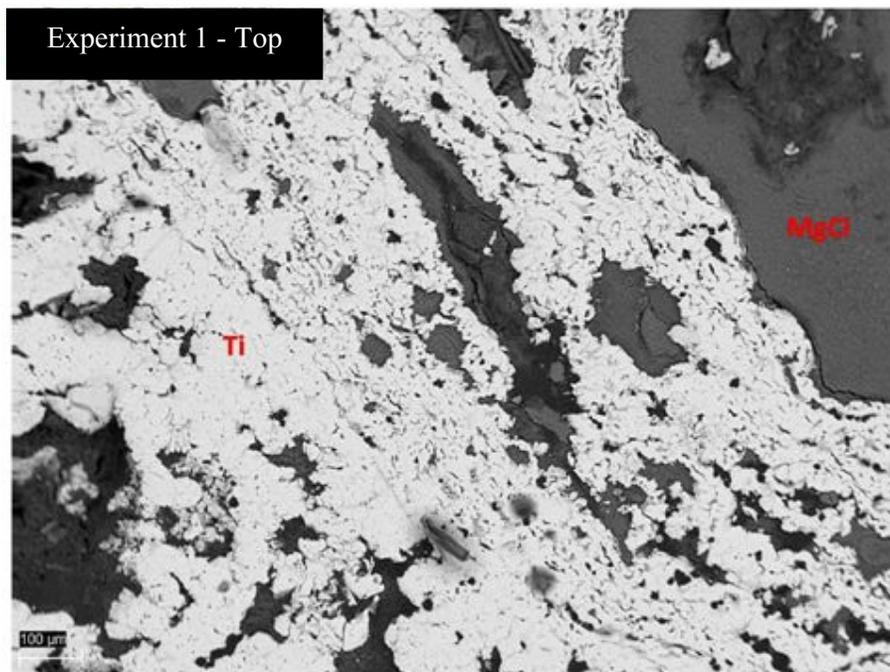


Figure 8- Backscattered electron image illustrating the porous texture of the Ti-metal in the top part of Experiment 1. The scale bar represents 100 μm .

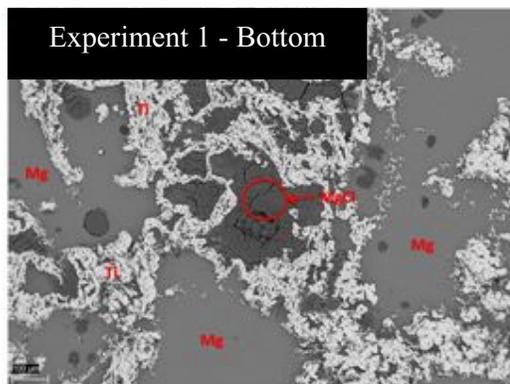


Figure 9- Backscattered electron image illustrating Ti-metal, Mg-metal and Mg-chloride as observed in the bottom part of Experiment 1. The scale bar represents 100 μm .

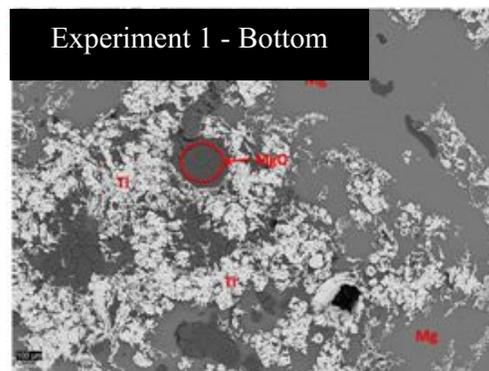


Figure 10- Backscattered electron image illustrating Mg-oxide formation in the bottom part of Experiment 1. The scale bar represents 100 μm .

Images of samples taken from the bottom of the crucible of Experiment 1 show an unreacted magnesium metal phase as well as phases of titanium metal, magnesium chloride and magnesium oxide.

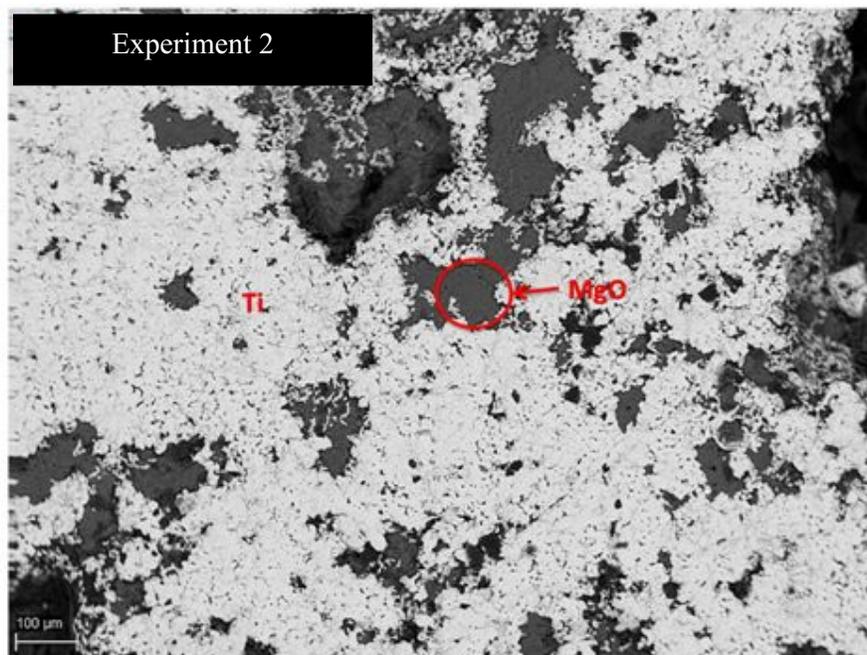


Figure 11- Backscattered electron image illustrating Ti-metal and Mg-oxide in Experiment 2. The scale bar represents 100 μm.

Images of the samples taken from Experiments 2 and 3 show more massive Ti metal phases. This may be due to the higher operating temperature of these experiments that might have improved the separation of Ti from other products present in the reactor.

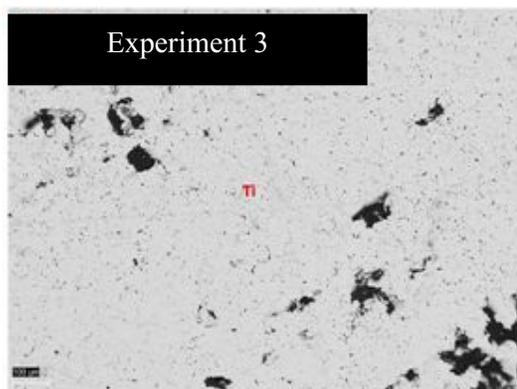


Figure 12- Backscattered electron image illustrating Ti-metal in Experiment 3. No other phases were observed. The scale bar represents 100 μm.

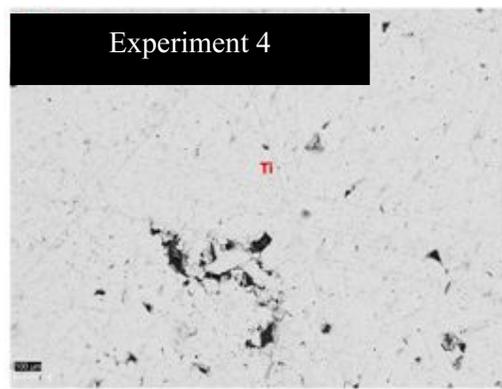


Figure 13- Backscattered electron image illustrating Ti-metal in Experiment 4. No other phases were observed. The scale bar represents 100 μm.

The sample from Experiment 4 also shows a massive Ti metal phase. The samples from Experiment 3 and 4 contained only the Ti metal phase indicating that less entrapment of magnesium metal and chloride took place.

Unreacted magnesium was found in the bottom part of the crucible; this might be as a result of uneven heating of the crucible. The bottom part of the crucible is the coldest part and magnesium that did not fully melt may become trapped by the growing layers of Ti sponge and therefore not be accessible to react with TiCl_4 . More efficient use of magnesium was observed during experiments with higher operating temperature set points, which supports the current theory.

Conclusion

The Mintek's laboratory-scale Kroll reactor for the production of titanium sponge was successfully operated. Although this reactor would need some modification to be able to better control the temperature uniformity throughout the reactor at least in the different product layers and the TiCl_4 flow rate, the initial operation results show that this reactor could be used to carry out a comprehensive research programme for the understanding of the Kroll process for the production of titanium sponge.

Approximately 1.4 kg and 0.6 kg of Ti sponge were produced respectively by magnesiothermic and calciothermic reduction of TiCl_4 .

The titanium grade of the sponge was relatively low since a significant quantity of magnesium metal and chloride was entrapped in this product. Based on preliminary sponge analysis, up to 85% of TiCl_4 was converted to Ti metal. It is believed that this conversion level is acceptable considering the size of the reactor. Conversion levels are affected by losses of TiCl_4 when venting the reactor to release pressure build-ups (maintain adequate operating pressure), the entrapment of reducing metal in the titanium sponge which is exacerbated at low operating temperatures and losses of Ti metal particles during product handling and leaching.

From limited observations carried out, it is believed that the operating temperature and reaction rates have a large influence on the sponge morphology. The influence of the type of reducing metal on the sponge morphology is not yet clear and should be investigated further.

Although milled samples analysed for high levels of magnesium, oxygen and other impurities, SEM images showed areas without these contaminating phases. Improving the separation of magnesium and magnesium chloride from the sponge would improve the grade of sponge produced.

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After obtaining her M.Sc. at the University of Stellenbosch, Lina joined Mintek in 2002 as a junior engineer in the Pyrometallurgical Division. She has since gained valuable experience in various ferrous and non-ferrous smelting campaigns. Lina currently hold the position of Senior Engineer and concentrates on the study and advancement of titanium metal production through current and novel technologies.