A feasibility study for high-temperature titanium reduction from TiCl₄ using a magnesiothermic process

S L Ivanov and D Zablotsky
Institute of Physics, University of Latvia (IPUL), Miera str. 32, Salaspils, LV-2169, Latvia
E-mail: ivanov@sal.lv

Abstract. The current industrial practice for titanium extraction is a complex procedure, which produces a porous reaction mass of sintered titanium particulates fused to a steel retort wall with magnesium and MgCl₂ trapped in the interstices. The reactor temperature is limited to approx. 900 °C due to the formation of fusible TiFe eutectic, which corrodes the retort and degrades the quality of titanium sponge. Here we examine the theoretical foundations and technological possibilities to design a shielded retort of niobium-zirconium alloy NbZr(1%), which is resistant to corrosion by titanium at high temperature. We consider the reactor at a temperature of approx. 1150 °C. Supplying stoichiometric quantities of reagents enables the reaction in the gas phase, whereas the exothermic process sustains the combustion of the reaction zone. When the pathway to the condenser is open, vacuum separation and evacuation of vaporized magnesium dichloride and excess magnesium into the water-cooled condenser take place. As both the reaction and the evacuation occur within seconds, the yield of the extraction is improved. We anticipate new possibilities for designing a device combining the retort function to conduct the reduction in the gas phase with fast vacuum separation of the reaction products and distillation of magnesium dichloride.

1. Introduction
The primary industrial process for producing metallic titanium is conducted by chlorination of enriched titanium ore and magnesiothermic reduction of titanium tetrachloride TiCl₄ in a steel vessel [1]. Under high temperature iron and nickel contained in the reactor walls and titanium form a liquid eutectic [2,3]. The erosion by titanium leads to a structural weakness of the vessel and contamination of the reaction mass, whereby 50-90% of the titanium in the vicinity of the walls is classified as ferrotitanium or scrap. Hence, the temperature of the process is limited to approx. 900 °C. The reduction of TiCl₄ proceeds via intermediate stages with formation of lower titanium chlorides. The system TiCl₄-TiCl₃-TiCl₂-TiCl-Mg-MgCl₂-MgCl₃ permits about 70 potential reaction pathways, the major ones (Figure 1) are determined by thermodynamics and reaction kinetics [4]. The first most probable phase comprises the reduction of vaporized TiCl₄ by magnesium to TiCl₂ and further as it requires the participation of just 2 molecules of initial reagents. The formation of lower chlorides is also permitted by way of secondary reactions of chlorides with Ti. The efficiency of the reduction hinges on the kinetics of multicomponent reactions connected by complex pathways in a multiphase environment, whereas the transport of reagents into and out of the reaction zones can be a limiting factor. Theoretical studies [5] show that the temperature range approx. 1200 – 1400 °C is more beneficial for the reduction to metallic titanium. Hence, the improvement of the magnesiothermic process requires a technological outline, whereby the titanium tetrachloride and magnesium would
interact at a higher temperature than in the current process resulting in a more favourable kinetics, whereas the alternative - electrochemical route [19] - is severely handicapped by high deposition potential of Ti, multivalence and insolubility of TiCl$_4$ in fused salts with associated technical difficulties.

![Figure 1](image1.png)

**Figure 1.** Favorable reaction pathways according to thermodynamics and reaction kinetics (solid lines – condensed phase, dashed – vapor phase).

2. **New reactor**

The use of niobium alloys offers a considerable increase of the operating temperature and enables rapid disposal of magnesium chlorides, which comprise more than 90% of the reaction products, by discharging them into a condenser (see also Figure 3, left). In the past the IPUL has accumulated experience with NbZr lithium test loops at high temperature (>1000 °C) under vacuum [6]. It is known that niobium is resistant to corrosion by magnesium vapor up to approx. 1150 °C [7]. Preliminary experiments [8] on magnesiothermic reduction of titanium tetrachloride up to 1100 °C in a test reactor made of NbZr alloy showed no corrosive degradation. This alloy is weldable and therefore suitable for constructing a reaction retort for magnesiothermic reduction in the temperature range 1200-1400 °C. Herein, we explore the theoretical benefits of a high-temperature 1150 °C magnesiothermic route and the potential technological framework to ensure dosed supply of reagents and withdrawal of by-products using fast switching valves to conduct the process predominantly in the gas phase [9, 10, 11]. The high chemical activity of titanium requires conducting all operations under inert gas or in vacuum. The conditions of the reaction are selected to ensure that the reduction proceeds in the gas phase to obtain high-quality metallic titanium as fine powder [12] and that the by-product magnesium dichloride is mostly vaporized. This will reduce the amount of time required to evacuate the reactor by distillation of MgCl$_2$ into the condenser.

![Figure 2](image2.png)

**Figure 2.** Left - saturated vapor pressure as a function of temperature for TiCl$_4$, Mg, MgCl$_2$, TiCl$_2$ and titanium; middle - enthalpy ($H_T - \Delta_f H^0_{298.15K}$) of 1M of reagents and products of magnesium-
the thermal reduction, right - the change of the velocity in the nozzle and of the pressure in the reactor during the supply of magnesium.

The saturated vapors of MgCl\(_2\) at 1150 °C in a 10L lab-scale experimental reactor would produce a pressure of 0.137 bar, whereas their total mass is 1.3g (0.0137 M). A 1.3g of TiCl\(_4\) and 0.333g of magnesium are supplied to produce this quantity of MgCl\(_2\) and 0.327 grams of metallic titanium in accordance with the generalized thermochemical reaction (Figure 1):

\[
\frac{1}{2} \text{TiCl}_4 + Mg \rightleftharpoons \frac{1}{2} Ti + MgCl_2 + \Delta H_T
\]  
(1)

Hess’s law states that the eventual change of enthalpy is independent of the reaction pathway. Hence, the standard enthalpy of a generic reaction is obtainable from the equation

\[
\Delta_r H^o_{T} = \sum_j v_j \Delta_f H^o_{298.15K}(B_j) - \sum_i v_i \Delta_f H^o_{298.15K}(A_i)
\]  
(2)

where \(\Delta_f H^o_{298.15K}(X)\) is the standard enthalpy of formation [13] for the products (\(B\)) and initial reagents (\(A\)), and \(v_j\) are the corresponding molar quantities. Since \(\Delta H > \frac{V}{\Delta p}\) to a sufficient accuracy (approx. ±1%) \(\Delta U \approx \Delta H.\) Per Kirchhoff's law the enthalpy \(H_T\) for reagent \(Z\) at temperature \(T\)

\[
(H - \Delta_f H^o_{298.15K})_Z = \int_{298.15K}^{T} C_p.Z(t) \, dt + \sum_i H_{a,z} \cdot X(T - T_{a,z})
\]

where \(C_p = \frac{dH}{dT}\) - heat capacity at constant pressure, \(H_a\) and \(T_a\) are latent heat and temperature for the \(a\)th phase change; \(X(x)\) is the Heaviside’s step function. The thermal effect of the reaction (1) at temperature \(T\), when the initial reagents (\(A\)) are supplied at \(T_{\text{TiCl}_4}\) and \(T_{\text{Mg}}\) (\(T_i\)) is obtainable from the equation

\[
\Delta H_T(T_{\text{TiCl}_4}, T_{\text{Mg}}, T) = \Delta_r H^o_{298.15K} + \sum_j v_j (H_T - \Delta_f H^o_{298.15K})_{B_j} - \sum_i v_i (H_{T_i} - \Delta_f H^o_{298.15K})_{A_i}
\]  
(4)

The enthalpies of the reactants and reaction products are shown in Figure 2, middle. The standard enthalpy of the reduction reaction is \(-239\) kJ/mol (per mole of Mg) [4,14]. At 1150 °C the heat of reaction is 258.5 kJ per mole of Mg or 3.54 kJ for 0.0137 M. Assuming the magnesium is supplied at 800 °C, a heat of 3 kJ needed for its evaporation will cool the 10-kg walls by just 0.3 °C. At 1150 °C the vaporized magnesium is reacted with TiCl\(_4\), which is injected at 25 °C. Under adiabatic conditions in the reaction zone the reaction products are heated to 2500 °C: magnesium dichloride is superheated vapor, whereas titanium is molten, resulting in a local fusion of titanium particulates. The growing pressure of MgCl\(_2\) and TiCl\(_4\) vapors facilitates the mass transport out of the reaction zone toward slightly cooler walls entraining the finely dispersed titanium particles and depositing them on the walls. Hence, the presence of titanium in the discharged condensate would testify of the insufficiency of the reaction stage. At the same time the heat of the reaction is insufficient to change the temperature of the massive reactor walls. Most of this heat is removed from the reactor during the distillation of the reaction zone. Hence, the overheating of the reactor and the difficulties associated with intense cooling of the retort as in the current industrial practice can be mitigated. Following vaporization of 0.0137 M of magnesium the pressure in the reactor reaches 0.163 bar. After completion of the reduction reaction the vapor pressure of MgCl\(_2\) is 0.137 bar. The distillation of the vapors into the condenser at 720 °C reduces the pressure to 43 Pa. Supplying the magnesium in excess of the stoichiometric ratio, the surplus will be discharged along with the by-product MgCl\(_2\).

2.1. Injection and vaporization of magnesium

A stoichiometric quantity \(n_{\text{Mg}}\) of molten magnesium can be injected hydraulically into the reactor from a supplying tank at approx. 800 °C via a magnesium feed line and a nozzle with a small aperture \(\sigma_N\) by opening a controlled heat resistant valve for a certain period of time. The ejection velocity \(v\) follows from the unsteady Bernoulli equation

\[
\frac{dv}{dt} = \frac{1}{\rho h} \left[ \Delta p - 0.5 \left( 1 + \zeta_N(Re) \right) \rho v^2 \right]
\]  
(5)

where \(\Delta p = \rho gh - p_V + P\) is the pressure difference at the nozzle comprising hydrostatic contribution, feed tank overpressure (\(P\)) and reactor pressure (\(p_V\)) (including magnesium surface tension); \(\zeta_N\) is the nozzle hydraulic resistance coefficient [15], \(Re = v^{-1} \tau \sigma_N - \text{Reynolds number}\). The
linear stability analysis [16] shows that at a sufficiently small aperture diameter $\sigma_N$ the liquid jet is susceptible to a Plateau-Rayleigh instability leading to its breakup into an ensemble of liquid droplets beyond a critical length $\sim 4.2\sigma_N \sqrt{We}$ [17] ($We = \rho u^2 \sigma_N \gamma$ – Weber number, $\gamma$ – liquid magnesium surface tension at approx. 800 °C). Estimates show that the mass loss of a single droplet due to a radiative heat transfer from the walls of the reactor is small (approx. 6%), hence, the necessary conditions for vaporization arise solely at the wall-droplet interface. In the worst-case scenario the heat transfer becomes impeded by an insulating vapor layer due to the Leidenfrost effect. The dynamics of vaporization (and pressure) of spheroidal droplets [18] in this case can be modeled by equation

$$\ln[V(t)V_0^{-1}] = -(\alpha_k + \alpha_r) \frac{T_{wall}-T_{sat}^*}{\delta \rho [r+e(T_{sat}^*-T)]} t, \quad \alpha_k = \eta \cdot \frac{|r+e(T_{sat}^*-T)|}{(T_{wall}-T_{sat})} \lambda^* D^{-1} \cdot \sqrt{g \delta \rho \sigma^*}$$

where $\alpha_k$ and $\alpha_r$ are the convective and radiative heat transfer coefficients, $V_0$ and $V$ – volume of a spheroidal drop at initial time and time $t$, $\delta$ – thickness of an oblate spheroid representing the droplet ($D$ – its diameter), $T_{sat}^*$ - vapor saturation temperature, $T_{wall}$ – wall temperature, $\langle T \rangle$ – average temperature of the droplet, $\rho$ and $\rho^*$ are magnesium liquid and vapor densities, $\lambda^*$ - vapor thermal conductivity, $G_p$ – liquid magnesium heat capacity, $r$ is the latent heat of vaporization (liquid-vapor phase change enthalpy), $g = 9.81 \text{ m}^2\text{s}^{-1}$. Figure 2, right shows the normalized dynamics of the magnesium jet velocity and the buildup of reactor pressure during injection through a nozzle with a diameter $\sigma_N = 0.2 \text{ mm}$ into the reactor with internal pressure of 50 Pa from a feed tank with a hydraulic head $h = 0.4 \text{ m}$ and overpressure $P = 0.2 \text{ bar}$. Here, the pressure of magnesium vapor with density $m_{Mg}/10 \text{ L}$ is used as the characteristic pressure and the steady-state outflow velocity at constant pressure in the reactor - as the characteristic velocity. The dispensing time $\tau_p$ required for supplying the predetermined amount $m_{Mg}$ of magnesium into the reactor is obtainable from eqn (5) and the relation

$$m_{Mg} = 0.25 \pi \sigma_N^2 \rho \int_0^\tau_p v(t) dt$$

(7)

For the given parameters $\tau_p$ is 2.3 sec.

2.2. Injection of titanium tetrachloride and reaction

In the next stage a corresponding stoichiometric amount of titanium tetrachloride TiCl$_4$ is injected through a narrow aperture into the reaction retort containing vaporized magnesium. Flowing through the feed line to the lid of the reactor the TiCl$_4$ will be heated by the channel walls. The estimations taking into account a possible thermal insulation yield a temperature in excess of 400 K for a TiCl$_4$ jet entering the chamber with magnesium vapours. In this case, the saturated vapour pressure of TiCl$_4$ is much greater than that of magnesium (Figure 3, left) resulting in rapid vaporization. During the expansion the vapour-liquid jet of TiCl$_4$ reacts with the magnesium vapours, heats up and disintegrates into droplets of liquid magnesium chloride containing solid titanium particles and TiCl$_2$. The reaction products are then deposited at the walls and bottom of the retort.

2.3. Removal of vapors of magnesium chloride from the reactor

Upon the completion of the reaction, all of the magnesium dichloride MgCl$_2$ and excess magnesium will remain in the gas phase in the reactor. As soon as the valve connecting the reactor to the condenser is opened, the vapors from the reactor are sucked into the condenser. The hydraulic resistance of this channel is the main obstacle for the vapor removal rate. The pressure drop in the channel is related to the mass transfer rate as

$$p_v(t) - p_{cond} = \left( \lambda L_{D_H} + \sum z_i \right) \cdot \frac{\rho(t) v(t)^2}{2}$$

(8)

where $p_v(t), \rho(t)$ are the vapor pressure and density in the reactor at a time moment $t$, $p_{cond}$ is the saturated vapour pressure of MgCl$_2$ in the condenser (at 720 °C), $L$ and $D_H$ are the length and the hydraulic diameter of the channel, $z_i$ denotes local hydraulic resistances [15], $v(t)$ is the vapor velocity in channel. With the diameter of the channel being 5 cm, length 2 m and with the cross-
section narrowing at the valve to 2.5 cm, the estimated time of vapor evacuation from the reactor into the condenser will be about 0.095 s.

2.4. Scenario of the reactor operation

Figure 3, right shows a tentative flow chart for a single cycle. The cycle duration includes the time of evaporation of the supplied magnesium, the time of the reaction, the precipitation of fine dispersed titanium on the walls, and the time of the distillation of volatiles into the condenser. The titanium is periodically spilled through the bottom hole by opening the shutter. The quantity of titanium per cycle per 10 L of reactor volume is equal to a cube with the edge 0.47 cm. Powder titanium can undergo electroslag remelting to produce ingots of titanium alloys.

![Figure 3](image)

**Figure 3.** Left - basic components of the proposed device for intensive production of titanium by cyclic magnesiothermic reduction from titanium tetrachloride; right – tentative flow chart of one operating cycle: (initial state) – vacuum, reactor temperature 1150 °C; (step 1) – injection of magnesium, 0.333g per 10 L of reactor volume, the pressure in the reactor increases to 0.163 bar; (step 2) – injection of 1.297 g TiCl$_4$ (per 10 L), the reaction proceeds rapidly with heat release, 1.302 g (per 10 L) of MgCl$_2$ vapors and 0.327 g (per 10 L) of solid titanium are formed in the reactor, the pressure is 0.137 bar; (step 3) – the outlet valve is opened, which connects the reactor to a cold evacuated chamber (condenser) with the temperature 720 °C (the vapor pressure is 48 Pa) to discharge MgCl$_2$; (end of cycle) – the cycle is completed after the valve is shut (closed), the pressure in the reactor is 50 Pa and the cycle can be repeated.

3. Conclusions

We attempted to predict how to utilize the technological advantage of the reaction occurring in the reactor at 1150 °C predominantly in the gas phase and how to realize the process using special equipment, i.e. high-temperature, quick-operating valves and gates or shutters. This implies a successive batch feeding of the reagents and the removal of volatiles after the reaction, making room for another reaction. In this case, the working space will be reduced only due to the titanium remaining in the reactor. Since in the gas phase titanium is formed as powder [12], then, apparently, it will be
possible to design a reactor with the periodic titanium powder spilling through the opening channel into a separate vessel outside the reactor and the furnace. Then the thermal reduction of titanium by magnesium can be assumed continuous. Currently a prototype of the reactor with operating temperature up to approx. 1200 °C, combined with the condensing unit, are being built to carry out experiments on the reduction of titanium tetrachloride with dosed supply of reagents and periodic distillation. Preliminary estimates indicate that this process could be economically viable in comparison with the current industrial practice, provided that a number of technical difficulties could be resolved. The design of the structural units supplying the reagents through the lid of the reactor including high-temperature fast-switching valves and protection of the nozzles from corrosive environment in the reactor chamber will be key.

References

[1] van Vuuren D S 2015 Direct titanium powder production by metallothermic processes *Titanium Powder Metallurgy* (Elsevier) 69–93

[2] Wartman F S, Baker D H, Nettle J R and Homme V E 1954 Some Observations on the Kroll Process for Titanium J. Electrochem. Soc. 101(10) 507-513

[3] Nagesh Ch R V S, Sridhar Rao Ch, Ballal N B, Krishna Rao P 2004 Mechanism of titanium sponge formation in the kroll reduction reactor *Metallurgical and Materials Transactions B* 35(1) 65-74

[4] Garmata V A et al. 1983 *Titanium* (Moscow: Metallurgiya) 559

[5] Olkhov Yu N, Ogurtsov S V et al. 1969 Thermodynamics of the titanium redox reaction from titanium tetrachloride by magnesium and the choice of optimal ways to intensify the titanium production *Investigations in Titanium Chloric Metallurgy* (Moscow: Metallurgiya) 302

[6] Ivanov S L, Foliforov V M, Platacis E et al. 1994 Special features of Electromagnetic Pump Investigations for Space Nuclear Reactors *Proceedings of 2nd International Conference of Energy Transfer in MHD-flow*. Aussois-France, 643-650

[7] Byalobzheskiy A V, Tsirlin M S, Krasilov B I 1977 *High-temperature corrosion and the protection of super-refractory metals* (Moscow: Atomizdat)

[8] Ivanov S L, Maiorov M M, Blumberg E, Zyk A A reactor for the accelerated magnesium exothermic reduction of titanium from titanium tetrachloride (in preparation)

[9] Leland J D 1996 Economically producing reactive metals by aerosol reduction JOM 48(10), 52-55

[10] Hansen D A, Gerdemann S J 1998 Producing titanium powder by continuous vapor-phase reduction JOM 50(11), 56-58

[11] Sohn H Y 1998 Ti and TiAl powders by the flash reduction of chloride vapors JOM 50(9), 50-51

[12] Turner P C, Hartman A, Hansen J S, Gerdemann S J  Low cost titanium - myth or reality. DOE/Albany Research Center - 2001-086

[13] Lide D R 2003 *CRC Handbook of Chemistry and Physics*, 84th Edition (CRC Press)

[14] Tarasov A V 2003 *Titanium Metallurgy* (Moscow: Academkniga) p 328

[15] Idelchik I E 2012 *Handbook of hydraulic resistance* (U.S. Atomic Energy Commission, translated from Russian)

[16] Levich V G 1962 *Physicochemical hydrodynamics* (Englewood Cliffs, N.J.: Prentice-Hall)

[17] Lielausis O, Klyukin A A, Platacis E, Peinbergs J 2015 MHD experiments on liquid metal jet-like flows guided by curved substrates *Magnetohydrodynamics* 51(4) 685-694

[18] Kutateladze S S 1979 *Fundamentals of the theory of heat exchange* (Moscow: Atomizdat)

[19] Zhang W, Zhu Z, Cheng C Y 2011 A literature review of titanium metallurgical processes *Hydrometallurgy* 108 (2011) 177-188

Acknowledgments

This work was supported by the ERDF project No. 1.1.1.1/16/A/085 (Ti-REMOID).