Mechanically Activated Rutile and Ilmenite as the Starting Materials for Process of Titanium Alloys Production

Marcela Achimovičová, Christoph Vonderstein and
Bernd Friedrich

Abstract

The consumptive conventional process of titanium alloys production needs new innovative processes. As starting materials for aluminothermic reduction, natural TiO_2 and $FeTiO_3$ concentrates can be used. The keynote of the present chapter is mechanical activation as a pre-treatment step for these concentrates, which is realized by the milling in a vibratory industrial mill. Mechanically activated rutile ore used in aluminothermic reduction saved 30% booster expenses and decreased Cl_2 emissions. Mechanical activation of ilmenite and ilmenite/aluminum mixtures was performed, and the kinetics of subsequent hydrometallurgical production of synthetic TiO_2 by pressure and normal leaching were studied. New processes with the coupling of aluminothermic production of titanium alloys were proposed.

Keywords: rutile, ilmenite, anatase, mechanical activation, aluminothermy, leaching

1. Introduction

The production of titanium alloys by using the conventional process route is tremendously cost-intensive. Therefore, there is a huge endeavor for an alternative process route. In an aluminothermic reduction process, titanium oxide can be used to achieve a titanium alloy. The energy which is needed for the autothermic reduction is released by the reduction of titanium oxides as well as by metal oxides which are needed for the titanium alloy composition. As the energy released by these oxides is not sufficient, there are boosters like $KClO_4$ or CaO_2 that

are necessary. To reduce the amount of these boosters, the process of mechanical activation of titanium oxide (rutile, anatase, and ilmenite) is helpful.

1.1. Fundamentals of mechanical activation

According to Butyagin, the mechanical activation of solids is defined as an increase in reaction ability due to stable changes in solids structure [1]. Mechanical activation represents a multi-step process with changes in the energetic parameters and the amount of accumulated energy of solids in each step, and it is followed by the process of the defects accumulation, amorphization, formation of metastable polymorphous forms, and chemical reactions [2]. Depending on the number of solid phases involved, the solid-state reactions by mechanical activation are classified into single (homogeneous or inhomogeneous reactions) and multi-phase systems (heterogeneous reactions) (see **Table 1**). The homogeneous single-phase solid-state reactions are the defect reactions and inhomogeneous reactions are inter-solid diffusions with the concentration gradients. During the heterogeneous multi-phase solid-state reactions, the mass transport diffusion occurs across the phase boundaries, and one or more product phases are created [3–6].

1.2. Type of milling devices

The main problem for the technical application of the mechanical activation of minerals or ores is a suitable type of the mill. For initiation of mechanical activation, the impact load mechanism is required. This is performed in the vibratory mills that are manufactured in industrial scale. For mechanical activation examination only the lab-scale mills are commonly used. They are based on the pressure load mechanism due to centrifugal force of motion. An industrial eccentric vibratory mill (type: ESM 656–0.5 ks, Siebtechnik GmbH, Germany) for the mechanical activation of TiO_2 (rutile) and $FeTiO_3$ (ilmenite) concentrates was used (see **Figure 1**).

Type of reaction	Example
Homogeneous	$\gamma TiO_2 \xrightarrow{\beta} \alpha TiO_2$
Inhomogeneous	$\alpha TiO_2 \xrightarrow{\beta} \alpha TiO_{2-x}$
Heterogeneous	$2FeTiO_3 + 2.5 O_2 \rightarrow 2TiO_2 + Fe_2O_3$
	$TiO_2 + MgO \rightarrow MgTiO_3$
	$Ti + H_2 \leftrightarrow TiH_2$

α: rutile, β: anatase, and γ: amorphous TiO_2

Table 1. Solid-state reactions of the Ti systems carried out by mechanical activation.

Figure 1. Industrial eccentric vibratory mill (type: ESM 656–0.5 ks, Siebtechnik GmbH, Germany).

2. TiO$_2$ concentrate, rutile

As input material, rutile concentrate of Australian origin (95% TiO$_2$) is used with the following composition 57% Ti, 0.7% Zr, 0.7% Fe, 0.3% Nb, 0.2% Si, 0.1% Al, 0.1% Cr, <0.03% P, and <0.03% S.

2.1. Mechanical activation

In order to identify the reaction ability of the mechanically activated rutile at the subsequent metallurgical reaction, the mechanical activation degrees, I/I$_0$ are assigned. The ratios I/I$_0$ represent the X-ray diffraction intensities at the lattice plane (110) of rutile, whereas I$_0$ is the measured value for the untreated rutile (defined as 100% < 10 μm), and I is value for mechanically activated rutile. This ratio I/I$_0$ is a parameter that gives information about grain size, lattice defects, and solid-state reactions. The results in **Figure 2** showed the activation degree of the rutile concentrate milled for 1, 2, and 3 h was dependent on the specific energy consumption of milling. The degree of crystallinity, I/I$_0$ of rutile crystal structure, decreased from 0.7 to 0.25, with an increase in milling time [6].

2.2. Aluminothermic reduction process for titanium alloys production

The materials with a decreased crystallinity due to mechanical activation can be very useful for the aluminothermic reduction process to reduce the amount of boosters. An aluminothermic reaction presents the reduction of a metal oxide with aluminum as a reductant. The reduction is feasible when Al shows a greater chemical affinity for the non-metal element of the compound than the desired metal which should be reduced. Regarding the redution of TiO$_2$ with
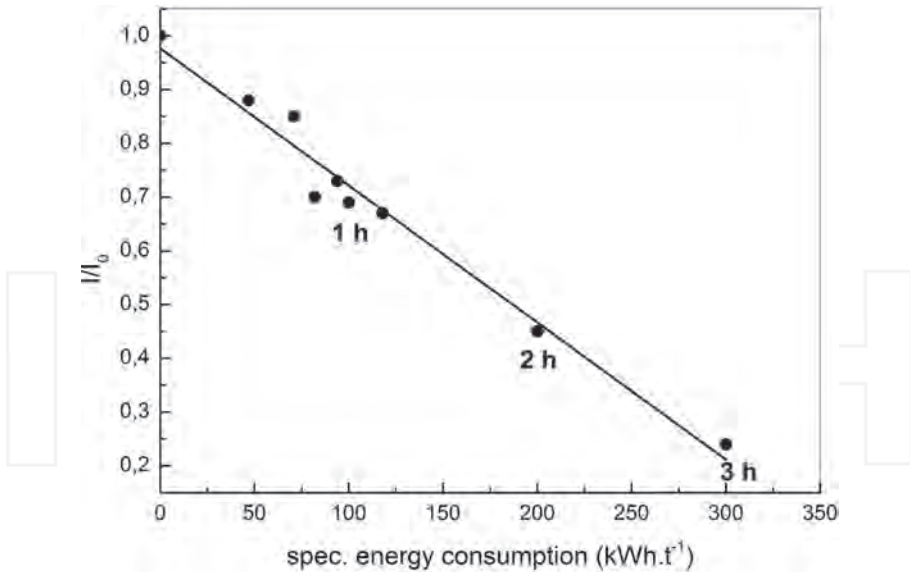
Figure 2. The mechanical activaction degree dependence on the specific energy consumption for rutile concentrate.

Al, the intrinsic heat of the reaction is not sufficient to maintain the self-sustained reaction [7]. Therefore, boosters (e.g., $KClO_4$, CaO_2) are added to reach the needed energy density. The modeling of the aluminothermic reaction mixture needs input parameters such as the required energy density, targeted adiabatic temperature, estimated heat losses, as well as aimed slag composition in order to improve the metal/slag separation. In order to reach the targeted temperature, changes in the mixture are not allowed to effect or vary the product alloy composition [7]. Because of little difference in the energy density from 50 to 100 $J.g^{-1}$ of aluminothermic reaction, the process window has to be exactly defined to supply slow propagation of reaction and early solidification. Rutile ore concentrate contains additional by-components which make the determination of the process conditions more complex. **Table 2** gives an overview of the reduction reactions of the by-components included in rutile concentrate [6].

The heats of these reactions differ significantly. Although the amount of these by-components are not very high, the released heats of each reaction have to be taken into account due to the above explained narrow process window. The reduction of several by-components is more favorable than the reduction of TiO_2 thus remaining within the metal phase. Therefore, the composition of the master alloy Ti-6Al-4V was carefully chosen, which corresponds to 60 wt.% of Ti, 24 wt.% of Al, and 16 wt.% of V. The investigations were focused on the definition of the required energy charging for the aluminothermic reaction with mechanically activated rutile to obtain a stable product. Important is the composition of the product, especially the contents of Ti, Al, and V and the by-components as well as the oxygen content in order proceed in the upcoming refining steps to achieve a valuable titanium alloy that can be produced cost-efficiently and can be used therefore in the car industry and other light-weight applications. It has to be balanced

Equations of the by-component reactions	$-\Delta H_R^0$ in kJ
$V_2O_5 + {}^{10}\!/\!_3\,Al \;\rightarrow\; 2\,V + {}^5\!/\!_3\,Al_2O_3$	1242.2
$SiO_2 + {}^4\!/\!_3\,Al \;\rightarrow\; Si + {}^2\!/\!_3\,Al_2O_3$	206.4
$Fe_2O_3 + 2\,Al \;\rightarrow\; 2\,Fe + Al_2O_3$	849.9
$Cr_2O_3 + 2\,Al \;\rightarrow\; 2\,Cr + Al_2O_3$	548.5
$ZrO_2 + {}^4\!/\!_3\,Al \;\rightarrow\; Zr + {}^2\!/\!_3\,Al_2O_3$	19.6
$Nb_2O_5 + {}^{10}\!/\!_3\,Al \;\rightarrow\; 2\,Nb + {}^5\!/\!_3\,Al_2O_3$	893.2
$MnO + {}^2\!/\!_3\,Al \;\rightarrow\; Mn + {}^1\!/\!_3\,Al_2O_3$	173.6

Table 2. Heats of reduction per mole of oxides of by-components in rutile ore.

out on how much booster can be saved by charging a reasonable mechanically activated rutile, minimizing the introduced energy for milling and maximizing the saved amount of booster [6]. Based on the promising results of the preliminary trials, further trials were conducted in small (8.4 kg of mixture) and mid-scale (18.2 kg of mixture) levels, with a variation in the reaction parameters such as time of mechanical activation of rutile concentrate (0, 1, 2, and 3 h), grain size of Al (90–300, 500–800, and 700–1200 μm), and $KClO_4$ addition to achieve energy density of 2400 and 2500 J.g^{-1} for the aluminothermic reaction. The selected range for variation of each reaction parameter is shown in **Figure 3**.
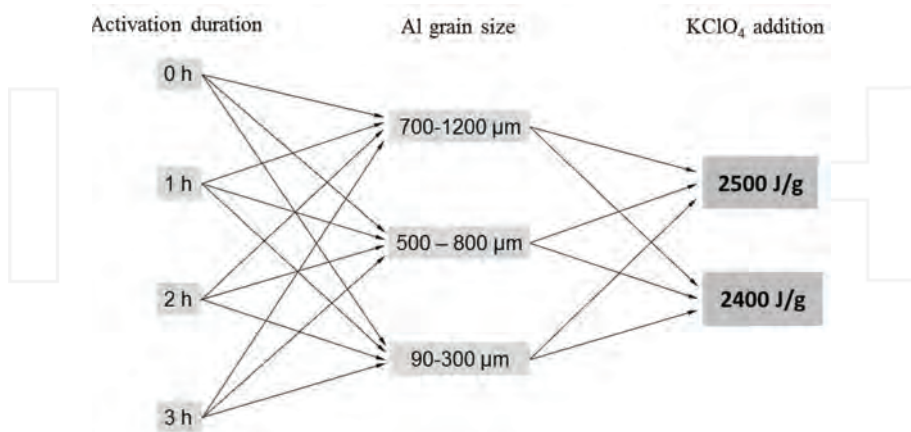

Figure 3. Variation of the trial parameters for the aluminothermic experiments [6].

The non-activated rutile (0 h) was used to compare the efficiency of the activation. The activation duration varies between 1 and 3 h. There are three types of Al grain sizes. Due to pre-trials, the two energy densities of 2400 and 2500 J.g^{-1} are used by KClO$_4$ addition [6]. This experimental setup indicates clearly that the trials with 2 h activation time and fine Al particles showed the best results according to the reaction time of the aluminothermic reduction and a good metal-slag separation. The metal composition was also the best in these trials. Small amounts of Fe and Si could be detected which would not interfere the final target alloy, Ti-Al6-V4 [6]. Because of avoiding the production of TiO$_2$ via chlorination, the savings were up to 50%, and because of mechanical activation, the use of KClO$_4$ decreased by 30% remarkably [6]. Due to the fact that lime is used as slag component to decrease the liquid temperature of the final slag, there are investigations to avoid the KClO$_4$ completely by using CaO$_2$ which will be reduced by Al to CaO and remains as slag component without producing any gas emissions. As the released heat by KClO$_4$ is nearly four times as high as the one by CaO$_2$, there is much more CaO$_2$ required to reach the needed energy density. Due to thermodynamic calculations, the amount of CaO should not exceed 50% because the liquid temperature of the slag will increase again and because of economic reasons, it should be used as sparsely as possible. As the energy density is decreased by mechanical activation, it is theoretical possible to reach a good amount of CaO in the slag and the needed energy density.

First trials were conducted with a 2 h mechanically activated rutile ore with CaO$_2$ as booster, varying the energy density. Besides the four trials which were conducted with an energy density from 2250 up to 2350 J.g^{-1}, the results were comparable to the experimental trials before. Due to the lower energy density in these trials, the metal-slag separation was not sufficient which resulted in high oxygen content in the alloy. The results for the oxygen content for the various trials varying the energy density can be seen in **Figure 4**.

A closer look to the trials with an energy density of 2450 J.g^{-1} shows that low oxygen contents can be reached. But there is also a large deviation for the oxygen content. This leads to the
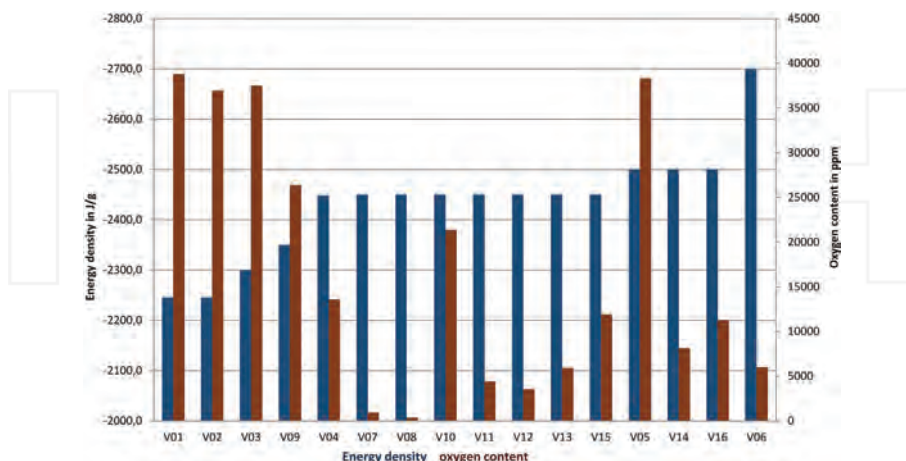

Figure 4. The various aluminothermic trials of the mechanically activated rutile for 2 h and CaO$_2$ as a booster.

assumption that the oxygen may not be completely diluted. Instead, there could be small oxide particles in the metal fraction which is a result of the slag-metal separation. Further investigations have to be performed. Therefore, a bigger-scale experiment to improve the separation needs to be done as well. Remelting this material in a vacuum induction furnace with a special ceramic crucible will be investigated to homogenize the material.

Mechanically activated rutile ore can be used for aluminothermic reduction to produce a titanium master alloy. $KClO_4$ can be used, as well as CaO_2 as booster. In this regard, a remarkable amount of KCl gas could be avoided. Using just CaO_2 as a booster could avoid the production of KCl completely.

3. $FeTiO_3$ concentrate, ilmenite

The beneficiation of ilmenites requires pyrometallurgical or chemical process steps to separate the iron content of approximately 30%. There are some methods of iron separation from $FeTiO_3$, which vary in their technical and energy demands. The chemical sulfate process, with H_2SO_4 at < 220°C, yielding TiO_2 in pigment quality, is difficult and complex because of the low solubility of ilmenite in H_2SO_4 [3]. Nevertheless, for the production of synthetic TiO_2 concentrates except for the pyrometallurgical processes [8, 9], the connected pyro- and hydrometallurgical processes [10–13] were developed. One possibility of the direct hydrometallurgical processing of $FeTiO_3$ is its pre-treatment by mechanical activation [14]. The studies on the solubility of $FeTiO_3$ after mechanical activation using different mills for ultrafine grinding such as vertical ball mills (attritors), planetary ball mills, and drum mills have been published, in which the structural changes of $FeTiO_3$ without technical applicability was focused [15–17]. In general, due to mechanical activation, the solids are exposed to high mechanical stress, which is responsible for their specific surface area increase, the crystalline structure defects formation and leads to the enthalpy increase. Hence, mechanically activated solids and minerals with low solubility are more leachable in subsequent hydrometallurgical process [18]. The application of mechanical activation of $FeTiO_3$ by energy-efficient milling as a pre-treatment step in the hydrometallurgical process of synthetic TiO_2 concentrates production might be a new realization to utilize such TiO_2 materials (~95%) in aluminothermic Ti alloys generation.

3.1. Mechanical activation and the kinetics of subsequent hydrometallurgical production of synthetic TiO_2 by pressure leaching

The investigations were carried out with $FeTiO_3$ concentrates (>95% $FeTiO_3$, <5% SiO_2) of Russian origin (GMD, Mineral Trade Company). The chemical composition was as follows: 34.43% Fe, 30.02% Ti, 0.76% Si, 0.47% Mg, 0.42% Al, 0.34% Mn, 0.11% Zn, 0.09% Ca, 0.07% Cr, 0.06% Co, 0.03% Ba, 31.63% O, and 1.57% insoluble rest.

For determination of the optimal milling conditions, a parameter study was done: mill feed quantities varied from 100 to 300 g/charge, activation times ranged from 15 to 60 min, the amplitude of inhomogeneous vibrations was 20 mm, and the revolutions of the motor of the mill, 960 min^{-1}, were constant. The steel balls of 30 mm diameter were applied. Activation degrees

and the ratios I/I_0 at lattice plane (104) of $FeTiO_3$ after and before mechanical activation as a function of mechanical activation time are shown in **Figure 5**. It is obvious that the ilmenite structure is strongly strained by the mechanical activation.

The leaching of mechanically activated $FeTiO_3$ was performed in an autoclave, volume 2 l (Deutsch & Neumann, Germany). The following conditions were used: initial H_2SO_4 concentration of 10–30%, temperature of 100–150°C, leaching time of 15–90 min, Fe addition of 6–12%, the solid to liquid ratio of 50–200 g.l^{-1}, and stirring rate of 250 min^{-1}.

The influence of the activation time of $FeTiO_3$ on the TiO_2 extraction to the precipitation product is shown in **Figure 6**. The curve for the total Fe extraction in the product reflects the dissolution of $FeTiO_3$. The leaching tests confirm the dependence on the activation degree of $FeTiO_3$. A critical point is that, after 15 min of mechanical activation, most of $FeTiO_3$ is dissolved. This finding is extremely interesting from a technical point of view. The hydrolytic precipitation of TiO_2 is influenced by an initial dissolution accelerated with increasing activation.

At temperatures >50°C and a pH value >1.5, the hydrolysis of titanyl sulfate solution, $TiOSO_4$ to TiO_2, is triggered. In the investigated temperature range of 100–150°C, the dissolution of $FeTiO_3$ and the simultaneous precipitation of TiO_2 take place in parallel.

The leaching time was varied in a range from 15 to 90 min. A general fact is that the dissolution rate of $FeTiO_3$ is fast. **Figure 7** shows the dissolution of ~64% $FeTiO_3$ (corresponding to the dissolution of Fe) during 30 min of leaching at 120°C. By increasing the reaction temperature to 150°C, ~86% of $FeTiO_3$ dissolves during 30 min of leaching. It results from **Figure 7** that the leaching time had a relatively low effect on the hydrolysis. After 60 min of leaching, the recovery
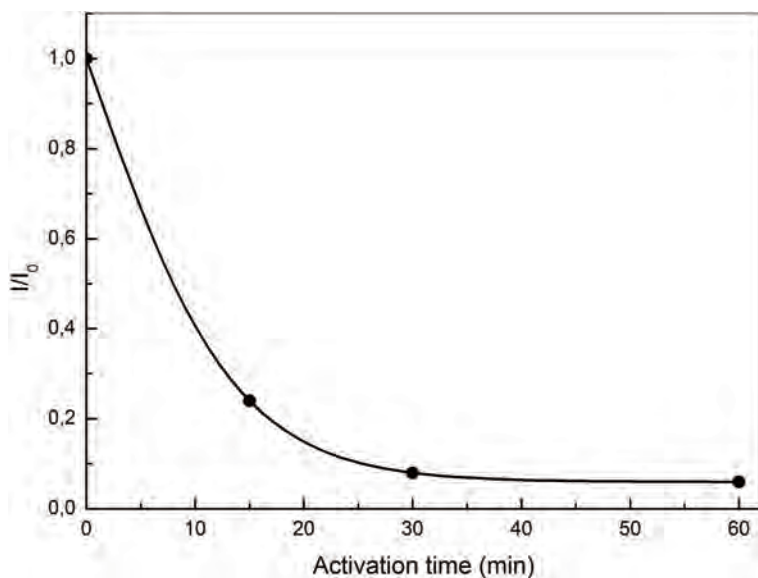

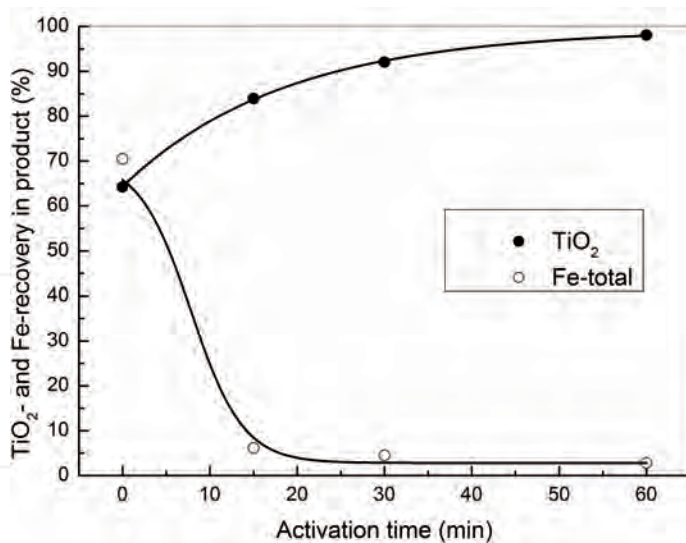**Figure 5.** Activation degrees I/I_0 of $FeTiO_3$ versus mechanical activation time.

Figure 6. Influence of the mechanical activation time of $FeTiO_3$ on the precipitation of TiO_2; leaching temperature: 150°C, s/l ratio: 50 g.l^{-1}, leaching time: 60 min, H_2SO_4 : 30%, and Fe powder: 12%.
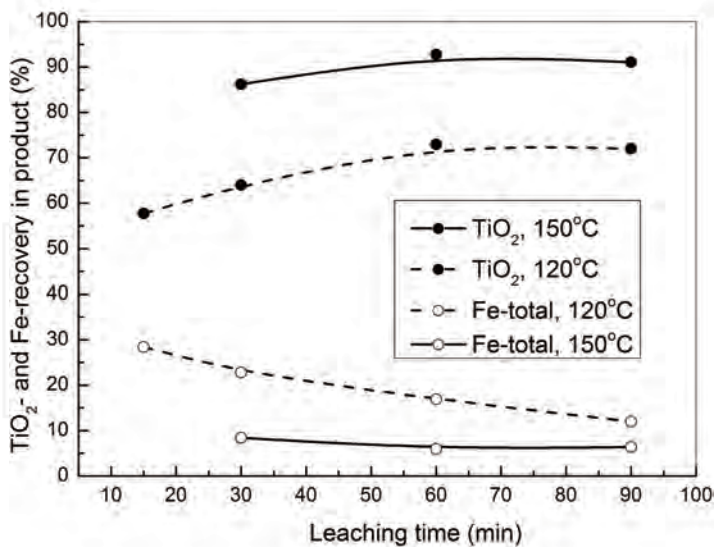

Figure 7. Influence of the leaching time and the temperature on the precipitation of TiO_2; s/l ratio: 50 g.l^{-1}, mechanical activation time: 15 min, H_2SO_4: 30%, and Fe powder: 6%.

of precipitated TiO_2 achieved ~93% and the content of Fe in TiO_2 decreased to <6%. The synthetic TiO_2 product assigned a relatively high purity. By decreasing the leaching temperature from 150 to 120°C, the obtaining of the high-quality synthetic TiO_2 concentrate is impossible [19].

It was detected that the addition of Fe powder, used as a reduction agent, influences the initial rate of $FeTiO_3$ dissolution (86% with an addition of 6% Fe and 89–92% with an addition of 12% Fe) and after a leaching time of 60 min, the influence of the Fe additive is no longer identifiable [19].

Sulfate process requires ~2 tons of concentrated H_2SO_4 per 1 ton of $FeTiO_3$ for digestion. Subsequently, the generated digestion cake is leached with H_2O by pH < 1.5. Therefore, the direct leaching of mechanically activated $FeTiO_3$ carried out by a described procedure requires a solid/acid ratio of 1:2 at least, which corresponds to 10% H_2SO_4 and 77% dissolution of $FeTiO_3$ (mechanically activated for 15 min) after 60 min of leaching, at 150°C, with addition of 10% Fe. By increasing the initial acid concentration to 20%, which corresponds to a ratio of 1:4, $FeTiO_3$ dissolves to 89%. For technical dimensioning, the ratio of ilmenite to acid should be <1:4. An excessively high amount of acid would complicate the hydrolytic conditions.

The solid contents from 50 to 200 g.l^{-1} were investigated. In order to show the influence of mechanical activation on the leaching of $FeTiO_3$ with different s/l ratios, two test series with activation times of 15 and 30 min were carried out. As expected, the residual Fe content in the product increases to 7% with increasing s/l ratio to 200 g.l^{-1} at a higher activation time. That means the activation time, 15 min, is sufficient to achieve 92% of dissolution of $FeTiO_3$ with s/l ratio of 200 g.l^{-1} and with 30% H_2SO_4 at 150°C.

According to literature, the research on the leaching of the mechanically activated ilmenites demonstrated no technical applicability. For various types of the mills, the milling times of up to 200 h were used, and low s/l ratios (only 10 g.l^{-1}) for the leaching process were employed [15–17, 20, 21]. The operating conditions determined in this investigation fulfill the requirements for a technical implementation of the process for the production of a synthetic TiO_2 product (95.23% TiO_2, 3.32% Fe_2O_3, 1.7% SiO_2, 1.2% CaO, 0.34% Al_2O_3, 0.007% P_2O_5, and 0.004% ZrO_2), which is suitable for use in aluminothermic alloys production. **Figure 8** shows the process flowsheet on the coupling of hydrometallurgical processing of $FeTiO_3$ into synthetic TiO_2 concentrate (anatase) with the aluminothermic production of TiAl alloys.

The energy required per ton of synthetic anatase is expected to be 506 kWh. Based on current costs for energy, this corresponds to approximately 212 €/t of synthetic anatase. This investigated pre-treatment of ilmenite with mechanical activation and leaching enables new cost-effective production methods for titanium-based alloys. So far, only high-purity rutile pigments have been used for the aluminothermic production of TiAl alloys [7, 22]. At 95% TiO_2, the synthetic TiO_2 concentrate (anatase) that we produced meets the requirements for aluminothermy.

3.2. Mechanical activation with metal addition and the kinetics of subsequent hydrometallurgical production of synthetic TiO_2 by normal leaching

Mechanical activation of $FeTiO_3$ with Al powder in the stoichiometric ratio 1:2 caused its mechanochemical reduction already after 120 min. The product phases found on the thermodynamic calculations with 1100–1700°C (Al_2O_3, TiO, Fe_2Ti, and FeTi) have already appeared after 360 min of mechanochemical reduction. Such mechanochemical processing of $FeTiO_3$
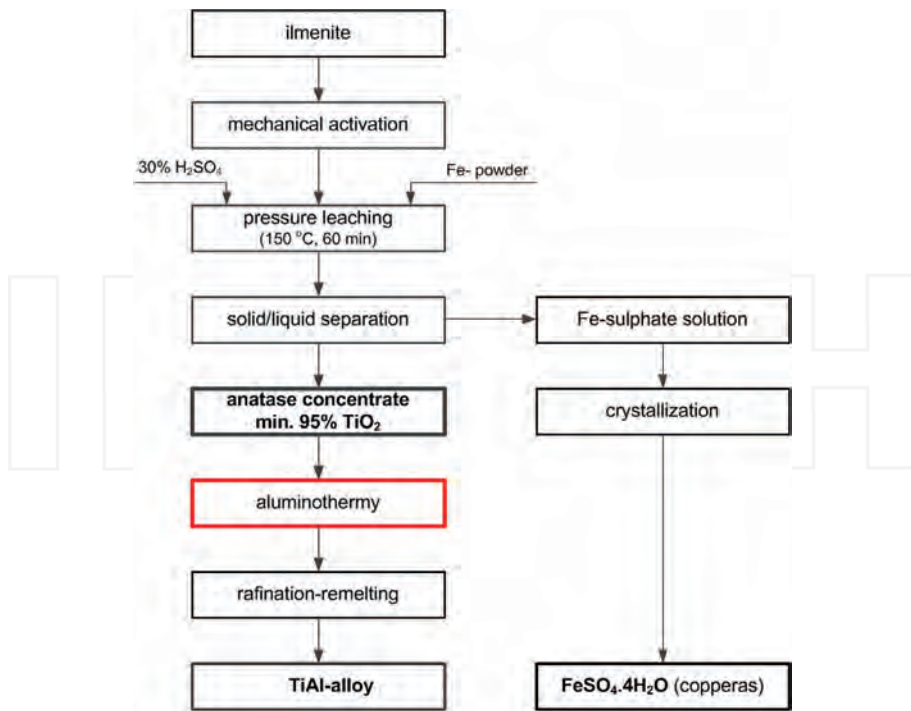
Figure 8. A process flowsheet of hydrometallurgical processing of $FeTiO_3$ connected with the aluminothermic production of titanium alloys.

concentrate decreases the temperature and subsequently the time of thermal reduction of $FeTiO_3$, which could be also used in the titanium alloys production [23]. For subsequent leaching in H_2SO_4 (40%) at 50°C, mechanically activated $FeTiO_3$ with Al in ratio 1:0.3 was tested. In this case, the necessary agglomerates of $FeTiO_3$/Al are created even after 15 min of mechanical activation. **Figure 9** shows the measured grain size distribution of the unmilled $FeTiO_3$ and the activated $FeTiO_3$/Al mixtures.

The SEM image in **Figure 10** shows the formed agglomerates. The contact pressure caused by the impact stress on the agglomerates during the second stage of ultrafine milling (agglomeration stage) leads to structures similar to briquettes with the highest bulk density [24, 25].

By leaching of agglomerated $FeTiO_3$/Al mixture with diluted H_2SO_4, the highly reactive atomic hydrogen (in nascent state) is created at the contact areas between $FeTiO_3$ and Al, which immediately reacts and causes a partial reduction of the quadrivalent titanium to trivalent titanium. A Ti^{3+}/Ti^{4+} dark violet to black solution is generated. The summation equation of the conversion of $FeTiO_3$ with diluted H_2SO_4 in the presence of hydrogen in nascent state is [24]:

$$2Fe(II)Ti(IV)O_3 + 5H_2SO_4 + 2H° \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2Ti^{3+} + 3SO_4^{2-} + 6H_2O \qquad (1)$$
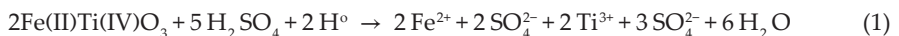
Figure 11 shows that the maximum Ti recovery of activated $FeTiO_3$ reaches 23%. Activated $FeTiO_3$/Al mixture shows a 53% Ti dissolution after only 15 min of activation.
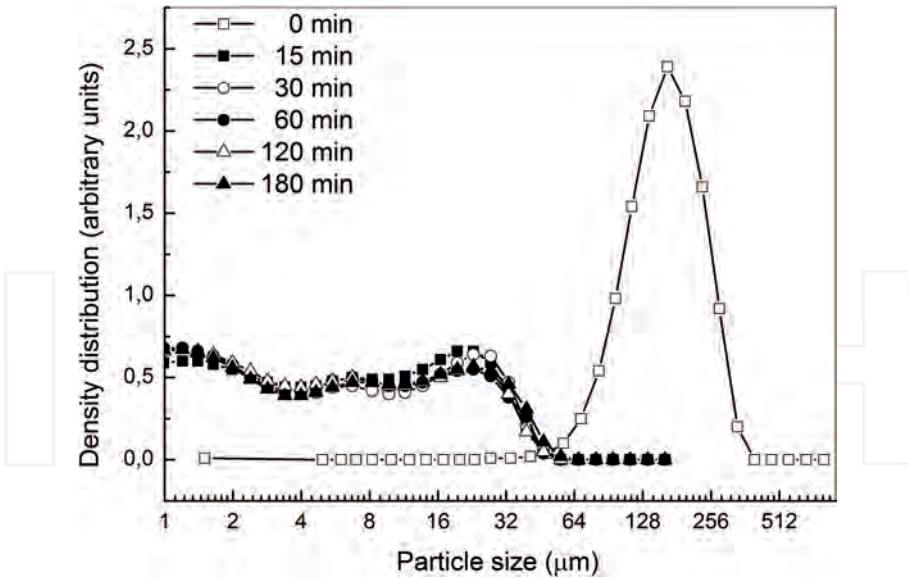
Figure 9. Grain size distributions of FeTiO$_3$/Al mixtures with various times of mechanical activation.
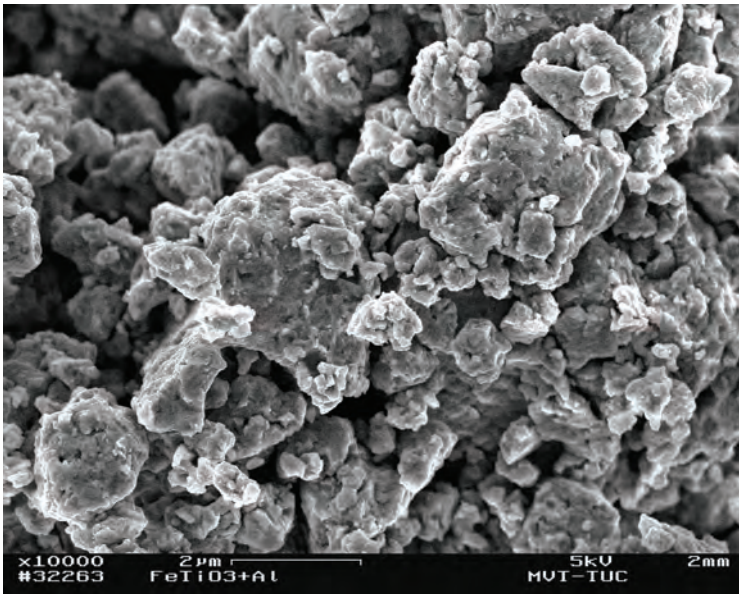

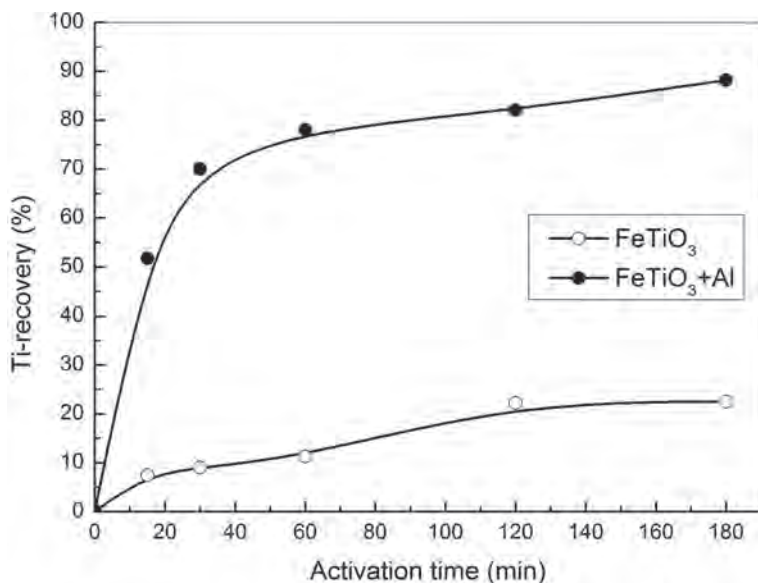**Figure 10.** SEM image of formed FeTiO$_3$/Al agglomerates.

Figure 11. Influence of mechanical activation time of FeTiO$_3$ and FeTiO$_3$/Al mixtures on Ti extraction during 60 min of leaching.

Investigations on the influence of the initial H$_2$SO$_4$ concentration on the leaching of FeTiO$_3$/Al mixture (150 g.l^{-1}) activated for 60 min, with the use of 30, 40, 50, or 60% H$_2$SO$_4$, show a maximum Ti recovery of 79% after a leaching time of 60 min and the use of 40% acid, corresponding to a solid/acid ratio of 1:3.3. With the increase of the initial H$_2$SO$_4$ to 50% (solids/acid ratio 1:4.3), dissolved Ti^{3+} partially hydrolyses, which causes the decrease of Ti recovery to 42%. For technical scale, the solid/acid ratio should be <1:4 because an excess H$_2$SO$_4$ complicates the conditions of subsequent TiO$_2$ hydrolysis. Ti recovery after 60 min of leaching is ~78% when milling charge of 200 g was used. With a further increase to 300 g/charge, the Ti recovery decreases to 69%. For 600 g/charge, the Ti-recovery reaches to 56%, which is still a high value. Ti recovery for the unmilled FeTiO$_3$ was 0.3% only. A check of the s/l ratio per liter showed that the optimal ratio was 150 g.l^{-1} of FeTiO$_3$/Al mixture. For technical processes, at least 300 g.l^{-1} must be feasible. **Figure 12** evidences that the leaching rate of FeTiO$_3$/Al mixture at temperature 50°C is very fast. After 5 min of leaching, the Ti recovery was 69% and after 60 min of leaching, almost 80% of Ti was leached out.

In **Figure 13**, the flowsheet of the described process for production of synthetic TiO$_2$ was proposed [26]. In an open agitator vessel, FeTiO$_3$/Al mixture is dissolved at a temperature of 50°C since the strong bond in the briquetted mixture follows the shrinking core model [26]. Undesirable metals, Fe and Al, can be crystallized as a mixture of Fe, Al sulfates at temperature < 15°C. Ti(OH)$_3$ precipitates during hydrolysis and by calcination oxidizes to TiO$_2$ (anatase) with the following composition: 99% TiO$_2$, 0.59% Fe$_2$O$_3$, <0.1% Al$_2$O$_3$, <0.2% SiO$_2$, <0.03 ZrO$_2$, and 0.01% Cr$_2$O$_3$.
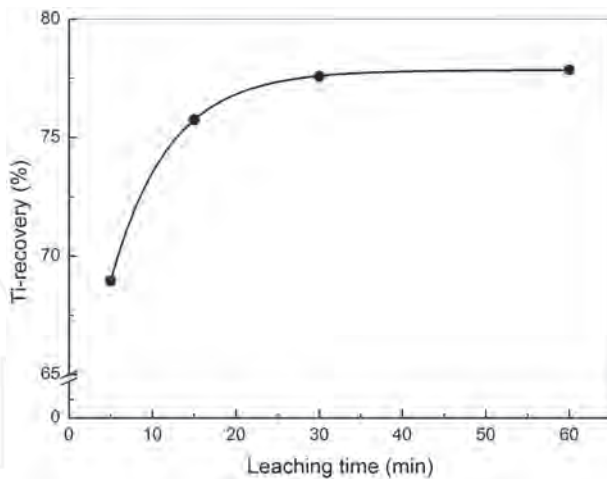
Figure 12. Influence of leaching time on Ti extraction of mechanically activated $FeTiO_3$/Al mixtures for 60 min with 40% H_2SO_4 and s/l ratio as 150 g.l^{-1}.
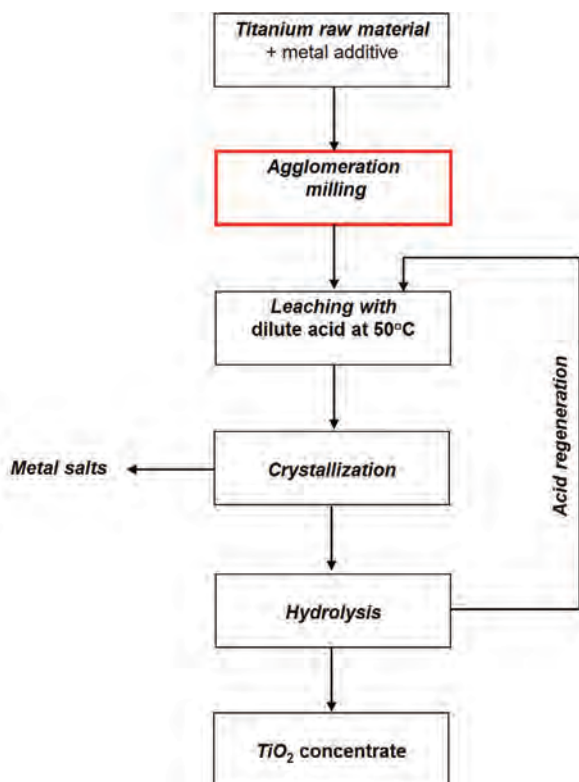

Figure 13. The flowsheet of a proposed process for production of synthetic TiO_2.

4. Conclusion

New technological processes of using titanium oxide concentrates (rutile, ilmenite) as starting materials for titanium alloys production were proposed. The first one is based on mechanical activation of natural rutile concentrate with milling, which caused the reducing of booster ($KClO_4$) amount around 30% and saving expenses for previous chlorination in subsequent aluminothermic reductions. Promising steps to replace the $KClO_4$ could be observed but are still under further investigations. The second process produces synthetic TiO_2 (anatase) from mechanically activated ilmenite concentrates treated by pressure leaching in dilute H_2SO_4 at 150°C. The third process presents the improvement of the previous one because ilmenite concentrate can be hydrometallurgically processed to synthetic TiO_2 by normal leaching in dilute H_2SO_4 at 50°C. Ilmenite concentrate has to be pre-treated by mechanical activation with aluminum as a reducing agent which leads to formation of $FeTiO_3$/Al agglomerates and a new effective reaction mechanism of leaching. After the separation of iron and aluminum by means of crystallization, it is possible to extract synthetic TiO_2 as a raw material for aluminothermic production of titanium alloys.

Acknowledgements

Author details

Marcela Achimovičová[1,2]*, Christoph Vonderstein[3] and Bernd Friedrich[3]

*Address all correspondence to: marcela.achimovicova@tu-clausthal.de

1 Institute of Mineral and Waste Processing, Waste Disposal and Geomechanics, University of Technology-Clausthal, Germany

2 Institute of Geotechnics, Slovak Academy of Sciences, Košice, Slovakia

3 IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany

References

[1] Butyagin PY. Structure disordering and mechanochemical reactions in solid states. Uspechi Khimiji. 1984;**53**(11):1769-1789

[2] Boldyrev VV, Tkáčová K. Mechanochemistry of solids: Past, present, and prospects. Journal of Materials Synthesis and Processing. 2000;**8**(3):121-132. DOI: 10.1023/A:1011347706721

[3] Gock E, Kähler J, Vogt V. Produktionsintegrierter Umweltschutz bei der Aufbereitung und Aufarbeitung von Rohstoffen. In: Brauer H, editor. Handbuch des Umweltschutzes und den Umweltschutztechnik. Vol.2. Berlin-Heidelberg-New York: Springer; 1996. pp. 79-237

[4]   Gock E, Jacob KH. Direkter Aufschluß von Rutil mit Schwefelsäure. Erzmetall. 1980;**33**(6): 308-314

[5]   Gock E, Szantho E. Laugung von Rutil nach mechanischer Aktivierung in einer Schwingmühle. Erzmetall. 1970;**23**:165-168

[6]   Hassan-Pour S, Vonderstein C, Achimovičová M, Vogt V, Gock E, Friedrich B. Aluminothermic production of titanium alloys (Part 2): Impact of activated rutile on process sustainability. Metallurgical and Materials Engineering. 2015;**21**(2):101-114

[7]   Stoephasius JC, Friedrich B. Modelling of metallothermic reactions—Impact of energy effects on the calculation of the reaction mixture. Erzmetall, World of Metallurgy. 2004;**57**(4):217-224

[8]   Noda T. Titanium from slag in Japan.The Journal of the Minerals, Metals and Materials Society. 1965;**17**(1):25-32

[9]   Lee HY, Poggi D. Mine, mill and smelting complex at Richards Bay, South Africa. The Metallurgical Society of CIM. 1978;**Annual**:93-96

[10] Berkovich SA. Recovery of titanium from ores. US patent 3903239. 1975

[11] Duyvesteyn W, Sabachy B, Verhulst D, Edmund V, Westsells PG. Processing titanifer-rous ore to titanium dioxide pigment. WO Patent 2001/00531 A1. 2001

[12] Thomas JB. Titanium dioxide pigment production from ilmenite. EU Patent 0186370. 1985

[13] Lakshmanan VI, Sridhar R, Rishea MM, Joseph DE, Laat R. Production of titanium metal from titanium-bearing ores involves leaching and selective removal of iron values by solvent extraction. US Patent 2001/007646-A1. 2001

[14] Gock E. Erzeugung von synthetischem Anatas aus Ilmeniten mit Dünnsäure. DE patent 3635010 A1. 1986

[15] Welham NJ, Llewellyn DJ. Mechanical enhancement of the dissolution of ilmenite. Minerals Engineering. 1998;**11**(9):827-841 DOI: 0892-6875(98)00070-3

[16] Li C, Liang B, Guo LH, Wu ZB. Effect of mechanical activation on the dissolution of Panzhihua ilmenite. Minerals Engineering. 2006;**19**(14):1430-1438. DOI: 10.1016/j.mineng. 2006.02.005

[17] Sasikumar C, Rao DS, Srikanth S, Mukhopadhyay N, Mehrotra SP. Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H_2SO_4. Hydrometallurgy. 2007;**88**(1-4):154-169. DOI: 10.1016/j.hydromet.2007.03.013

[18] Baláž P. Extractive Metallurgy of Activated Minerals. 1st ed. Amsterdam: Elsevier; 2000. p. 292

[19] Achimovičová M, Hassan-Pour S, Gock E, Vogt V, Baláž P, Friedrich B. Aluminothermic production of titanium alloys (Part 1): Synthesis of TiO_2 as input material. Metallurgical and Materials Engineering. 2014;**20**(2):141-154

[20] Li C, Liang B, Song H, Xu J, Wang X. Preparation of porous rutile titania from ilmenite by mechanical activation and subsequent sulphuric acid leaching. Microporous and Mesoporous Materials. 2008;**115**:293-300. DOI: 10.1016/j.micromeso.2008.01.045

[21] Tao T, Glushenkov AM, Chen Q, Hu H, Zhou D, Zhang H, Boese M, Liu S, Amal R, Chen Y. Porous TiO_2 with a controllable bimodal pore size distribution from natural ilmenite. CrystEngComm. 2011;**13**:1322-1327. DOI: 10.1039/C0CE00533A

[22] Stoephasius JC, Friedrich, B. Modelling of metallothermic reactions local reaction rates during aluminothermic γ-TiAl-Nb production. Erzmetall-World of Metallurgy. 2005;**58**(2):63-69

[23] Achimovičová M, Gock E, Turianicová E, Kostova NG, Velinov N, Kaňuchová M, Baláž P. Study of the mechanochemical reduction of ilmenite concentrate by addition of aluminum. Acta Physica Polonica A. 2014;**126**(4):867-870

[24] Gock E, Vogt V, Achimovičová M. Verfahren zum behandeln eisenhaltiger Titan-Rohstoffe. DE Patent 102014206776 A1. 2015

[25] Gock E, Vogt V, Achimovičová M. Procedures for treating ferrous titanium raw materials. International Journal of Research in Chemical, Metallurgical and Civil Engineering. 2016;**3**(1):49-53. DOI: 10.15242/IJRCMCE.IAE0316403

[26] Braun RL, Lewis AE, Wadsworth M. In-place leaching of primary sulfide ores: Laboratory leaching data and kinetics model. In: Aplan FF, editor. Solution Mining Symposium. Dallas: 103 AIME Annual Meeting; 1974. pp. 295-323