

ALUMINOTHERMIC PRODUCTION OF TITANIUM ALLOYS (PART 1): SYNTHESIS OF TiO₂ AS INPUT MATERIAL

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Abstract

This article reports on the hydrometallurgical production of synthetic anatase from ilmenite. Mechanical activation followed by pressure leaching facilitates the leaching of ilmenite and the separation of titanium/iron by means of the synchronous hydrolysis of anatase. At 95% TiO₂, the produced synthetic anatase fulfills the requirements for the aluminothermic production of titanium alloys.

Keywords: *ilmenite, mechanical activation, anatase process, pressure leaching*

Introduction

Titanium is one of the ten most commonly found elements in the earth's crust, together with O, Si, Al, H, Na, Ca, Fe, Mg, and K. The most abundant titanium mineral, ilmenite (FeTiO₃), is, together with rutile (TiO₂), a mass commodity of high availability.

The first step in the production of titanium metal is to gain pure TiO₂ products from ore concentrates containing ilmenite or rutile. The beneficiation of ilmenites requires pyrometallurgical or chemical process steps to separate the iron content of approx. 30%. The beneficiation of rutile to TiO₂ concentrates is mostly done physically.

Several different ways of separating the iron from ilmenite are known, which differ in their technical complexity and energy requirements. The chemical process is made difficult by the low solubility of ilmenite in sulphuric acid. For the production of pure TiO₂ concentrates from ilmenites, the classic sulphate process with concentrated H₂SO₄ at < 220°C, yielding TiO₂ in pigment quality, is too complex [1]. As a result,

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apart from strictly pyrometallurgical processes [2-4], combinations of pyrometallurgical and hydrometallurgical processes [5-28] were developed for the production of synthetic TiO_2 concentrates. These concentrates can be used as raw material for the sulphate process as well as for the chloride process. For the production of titanium metal, the TiO_2 content of approx. 90% is insufficient.

One possibility for the direct hydrometallurgical beneficiation of ilmenites is the pre-treatment of ilmenite concentrates by means of mechanical activation. First investigations on the solubility of ilmenites were presented in 1968 by Gock in a study on the mechanical activation of titaniferous magnetite [29]. Since the 1990s, more studies on the solubility of ilmenites after mechanical activation using different mills for ultrafine grinding such as vertical ball mills (attritors), planetary ball mills and drum mills have been published. The focus of the investigations was on the structural changes of ilmenite. Technical applicability was not the intention [30-38]. Mechanical activation in general means exposing solids to high mechanical stress, which exceeds the enlargement of the surfaces and causes defects in the crystalline structure leading to an increase in the level of enthalpy of the crystalline system. In many cases, the increase in the enthalpy strongly influences the reaction behaviour. The influence on the dissolving and leaching activities of mineral compounds with low solubility is important for hydrometallurgical processes. The scientific background is summarized in a few monographs [39-42].

The mechanical activation of ilmenites for direct hydrometallurgical production of synthetic TiO_2 concentrates by means of the energetically efficient vibration milling method could be a new concept for the use of this material in aluminothermic titanium alloy production. However, TiO_2 contents of at least 95% TiO_2 are required.

In the following, we will report on the reaction kinetics of mechanically activated ilmenite during the hydrometallurgical production of synthetic TiO_2 concentrates with anatase structure as input material for aluminothermic titanium alloy production [43].

Experiments

The material used was commercial ilmenite concentrate with 30.02% Ti, 34.43% Fe, 0.76% Si, 0.42% Al, 0.02% Cr, <50 ppm Th, <50 ppm U, 7 ppm Zr, <5 ppm P. The particle size was 100% <0.3 mm. The diffractometer analysis also showed content of hematite and quartz.

Mechanical activation took place in a full-scale eccentric vibratory mill [44-46] by Siebtechnik GmbH/Mühlheim Ruhr (ESM-656.0.5 ks), equipped with a 5 l satellite milling container for the treatment of smaller samples. With this setup it is possible to determine the energy requirements per ton of material input as well as the mill throughput for technical implementation. In order to determine the optimum activation conditions, parameter studies were carried out with mill feed quantities varying between 100 and 300 g per load and activation times ranging from 15 to 60 minutes. The amplitude or frequency of the mill was kept constant at 20 mm or 960 min^{-1} . Steel balls with a diameter of 30 mm were used.

The degree of activation was set as the ratio I/I_0 at lattice plane 104 of ilmenite after and before mechanical activation. Every degree of activation has a reproducible reaction kinetic behaviour.

The leaching tests were carried out in an agitator autoclave by Deutsch & Neumann GmbH, Berlin with a reaction volume of 2 L. The solvent used was diluted

H_2SO_4 . Stirring occurred at 250 min^{-1} and the temperatures were between 100 and 150°C . Further parameters were the initial acid concentration (10-30% H_2SO_4), the leaching time (15-60 min), Fe addition (6-16%) and the solids content per litre (50-200 g/l). An ICP-OES (Vista-MPX, Varian, Australia) was used for analytical measurements. The solutions as well as the precipitation products (anatase and copperas) were analysed. In addition, X-ray diffraction patterns (Philips X'Pert PW 3040 MPD, Germany) and scanning electron microscope image (Zeiss DSM 982 Gemini, Germany) were taken.

Results

The most important parameters influencing the hydrometallurgical processing of mechanically activated ilmenite are described below.

Influence of mechanical activation

The determination of the degree of activation was based on the treatment duration of a 100 g specimen. The determined degree of activation for the performed milling tests as a function of the milling time is shown in Figure 1. It is obvious that the ilmenite structure is strongly strained by the mechanical activation. The same behaviour was also observed in the case of thermal treatment of ilmenite in a muffle furnace [29]. At $> 800^\circ\text{C}$ in the presence of oxygen, ilmenite converts into rutile and hematite. This process is proven by the measurements at lattice plane 104.

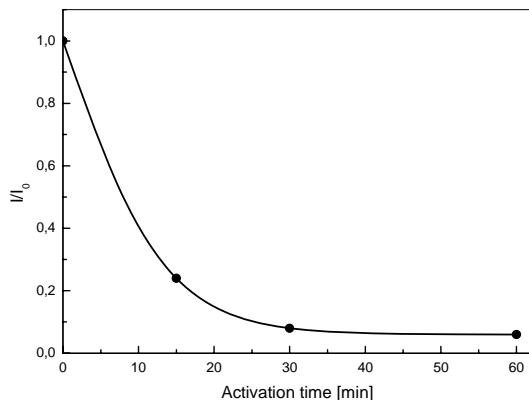


Fig. 1. Degree of activation I/I_0 of ilmenite as a function of the activation time measured at lattice plane 104 at $2\theta=32.7^\circ$

The influence of the activation time on the TiO_2 extraction in the precipitation product is shown in figure 2. The leaching tests confirm the dependence on the degree of activation. A critical point is that after a mere 15 minutes of activation most of the ilmenite has been dissolved. This finding is extremely interesting from a technical point of view. The hydrolytic precipitation of anatase is influenced by an initial solution accelerated with increasing activation.

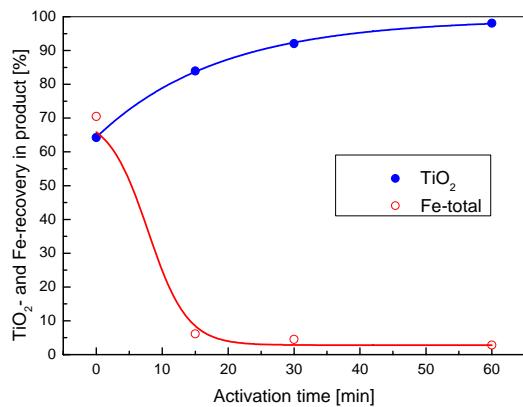


Fig. 2. Influence of the activation time of ilmenite on the precipitation of anatase; leaching temperature 150°C, solids content 50 g/l, leaching time 60 min, 30% H₂SO₄, 12% Fe-powder

Influence of temperature

At temperatures > 50°C and a pH value > 1.5 the hydrolysis from titanyl sulphate solutions to TiO₂ is triggered. In the investigated temperature range, the dissolution of ilmenite and the simultaneous precipitation of TiO₂ take place in parallel. If the hydrolysis conditions are less than perfect, a partial precipitation of TiO₂ will occur. The hydrolytic conditions are influenced positively, if the dissolution of ilmenite takes place at temperatures > 100°C under steam pressure in an autoclave.

The variation of the temperature in the range of 100-150°C yielded the reaction process shown in figure 3.

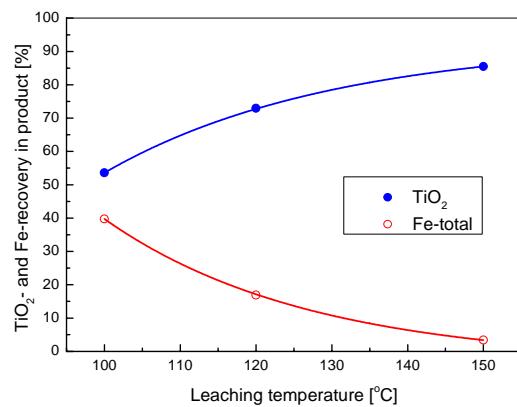


Fig. 3. Influence of the leaching temperature on the precipitation of anatase; solids content 50 g/l, 15 min eccentric vibratory milling, leaching time 60 min, 30% H₂SO₄, 6% Fe-powder

The curve for the total iron extraction in the product reflects the dissolution of the ilmenite. At a leaching temperature of 150°C and a leaching time of 60 minutes, approximately 86% of the ilmenite dissolves. Parallel to the dissolution of the iron, the titanium is being dissolved and the hydrolysis of the generated titanyl sulphate solution to anatase takes place following the almost complete dissolution of the ilmenite. At 150°C only traces of titanium remain in the solution. Under the same temperature conditions the amount of Fe powder, used as a reduction agent, was increased to 10%. Under these conditions, extraction was already largely achieved at a leaching temperature of 120°C. The TiO₂ extraction in the product is approx. 86% (see figure 4). The optimum reaction temperature is thus influenced by the amount of reduction agent. As proven in point: Influence of Fe-additive, the addition of Fe accelerates the initial reaction of the leaching.

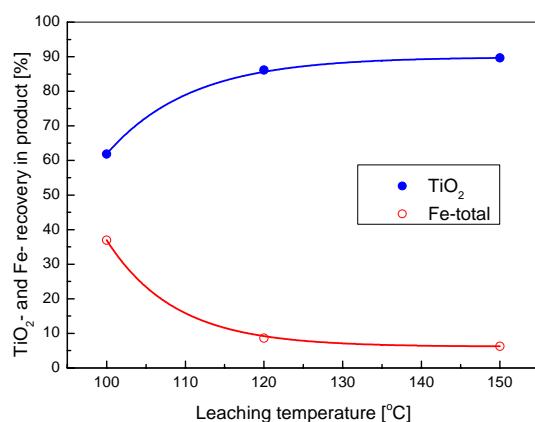


Fig. 4. Influence of the leaching temperature on the precipitation of anatase upon increasing the amount of reduction agent from 6 to 10% Fe-powder; solids content 50 g/L, 15 min eccentric vibratory milling, leaching time 60 min, 30% H₂SO₄

Influence of the initial acid concentration

The extraction of ilmenite using the sulphate process requires approximately 2 tonnes of concentrated sulphuric acid per tonne of ilmenite. The generated extraction cake is then leached with water. The content of free acid must guarantee a pH value < 1.5. As a consequence, the direct leaching of ilmenite performed here requires a solids/acid ratio of at least 1:2. Figure 5 shows the influence of the initial acid concentration on the solution of activated ilmenite using 10% acid. This corresponds to a solids/acid ratio of 1:2, and a 77% solution of ilmenite after a leaching time of 60 minutes. Increasing the initial acid concentration to 20%, this corresponds to a ratio of 1:4, the ilmenite almost completely dissolves. From a processing point of view, continuous operation requires keeping the acid in circulation and replacing the spent acid. It is in this way that the process acid always has a preparatory titanyl sulphate content.

As a consequence, it shows that the initial acid concentration has a direct influence on the rate of ilmenite dissolution. For technical dimensioning, the ratio of

ilmenite to acid should be $< 1:4$. An excessively high amount of acid would complicate the hydrolytic conditions.

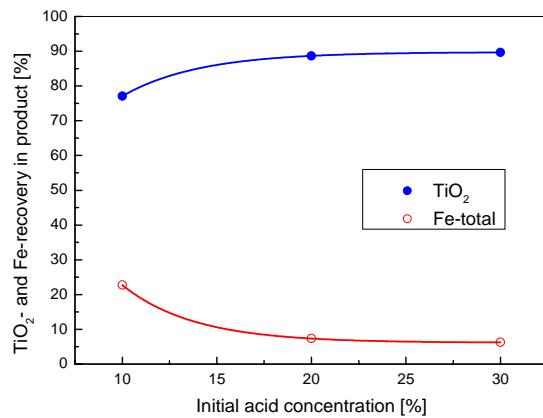


Fig. 5. Influence of the initial acid concentration on the precipitation of anatase; solids content 50 g/l, 15 min eccentric vibratory milling, leaching temperature 150°C, leaching time 60 min, 10% Fe-powder

Influence of the leaching time

The leaching time was varied in a range from 15 to 90 minutes. A general fact is that the dissolution of ilmenite takes place at a fast rate. Figure 6 shows the dissolution of ilmenite in a magnitude of approx. 64% (related to the dissolution of iron) at a leaching time of 30 minutes and a reaction temperature of 120°C.

When increasing the reaction temperature to 150°C, again, approx. 86% of the ilmenite dissolves after a leaching time of 30 minutes. Figure 6 also shows that the leaching time has a relatively low impact on the hydrolysis. After 60 minutes, approx. 93% of the anatase has precipitated and the Fe content in the anatase concentrate is reduced to < 6%. The generated product is a synthetic TiO₂ concentrate of relatively high purity.

If the temperature is lowered from 150°C to 120°C, it is impossible to produce a high-quality synthetic anatase concentrate.

Influence of the Fe-additive

As proven in point: Influence of temperature, regarding the influence of the leaching temperature, the addition of Fe influences the initial rate of the ilmenite dissolution. This correlation is shown in figures 3 and 4.

Figure 7 shows that after a leaching time of 60 minutes the influence of the Fe-additive is no longer identifiable.

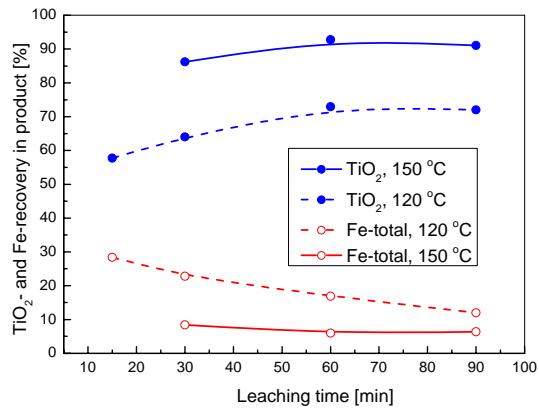


Fig. 6. Influence of the leaching time and the temperature on the precipitation of anatase; solids content 50 g/l, 15 min eccentric vibratory milling, 30% H_2SO_4 , 6% Fe-powder

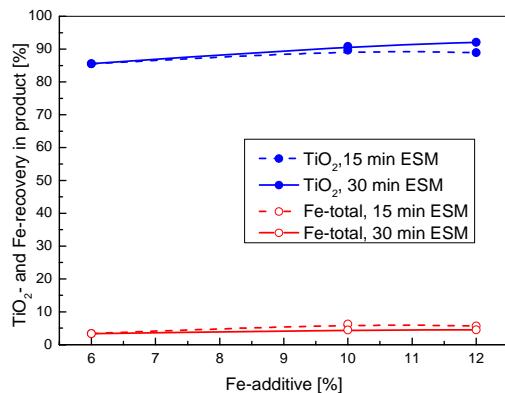


Fig. 7. Influence of the Fe-additive on the precipitation of anatase; leaching temperature 150 °C, 15/30 min eccentric vibratory milling, solids content 50 g/L, leaching time 60 min, 30% H_2SO_4

Influence of the solids content

Solids content between 50 and 200 g/L were investigated (Figure 8). In order to show the influence of mechanical activation on the leaching with different solids contents of FeTiO_3 , two test series with milling times of 15 and 30 minutes were carried out.

As expected, the residual iron content in the product increases with increasing solids content per litre at a lower activation time (<15 minutes). That means the ilmenite dissolves at a lower rate. For the technical process, this result is disadvantageous.

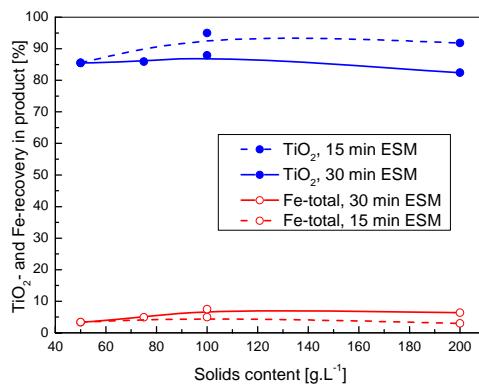


Fig. 8. Influence of the solids content on the precipitation of anatase; leaching temperature 150°C, 15/30 min eccentric vibratory milling, 30% H₂SO₄, 6% Fe-powder

Products

Table 1 shows the composition of the products produced using this anatase process: synthetic anatase and copperas.

Table 1: Composition of the products produced using the anatase process: synthetic anatase and copperas

Specimen	Al ₂ O ₃ [%]	CaO [%]	Fe ₂ O ₃ [%]	P ₂ O ₅ [%]	SiO ₂ [%]	TiO ₂ [%]	ZrO ₂ [%]
Anatase	0.34	1.20	3.32	0.007	1.70	95.23	0.004
Copperas	0.88	0.32	52.48	n.d	0.76	0.45	0.015

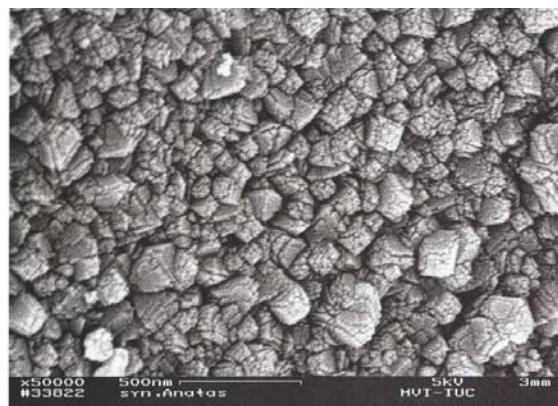


Fig. 9. Scanning electron microscope image of the produced synthetic anatase

A scanning electron microscope image of the synthetic anatase shows a narrow particle size distribution with an x_{50} value of 0.99 μm , (see figure 9). The X-ray analysis of the anatase product (JCPDS 021-1272) (see figure 10) shows traces of rutile. The

crystallised copperas, shown in the X-ray diffraction pattern in figure 11, is characterised by high purity. It is the compound $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (JCPDS 016-0699).

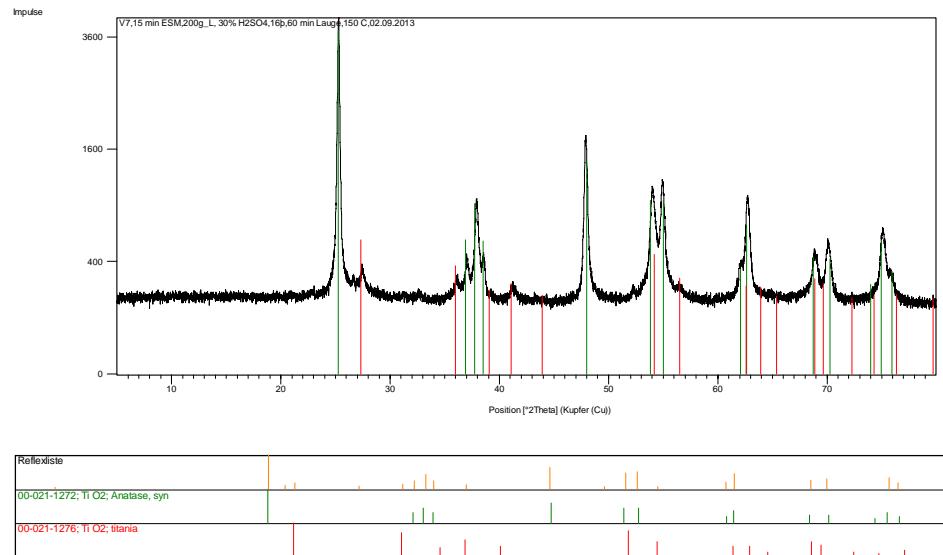


Fig. 10. X-ray diffraction pattern of the produced synthetic anatase

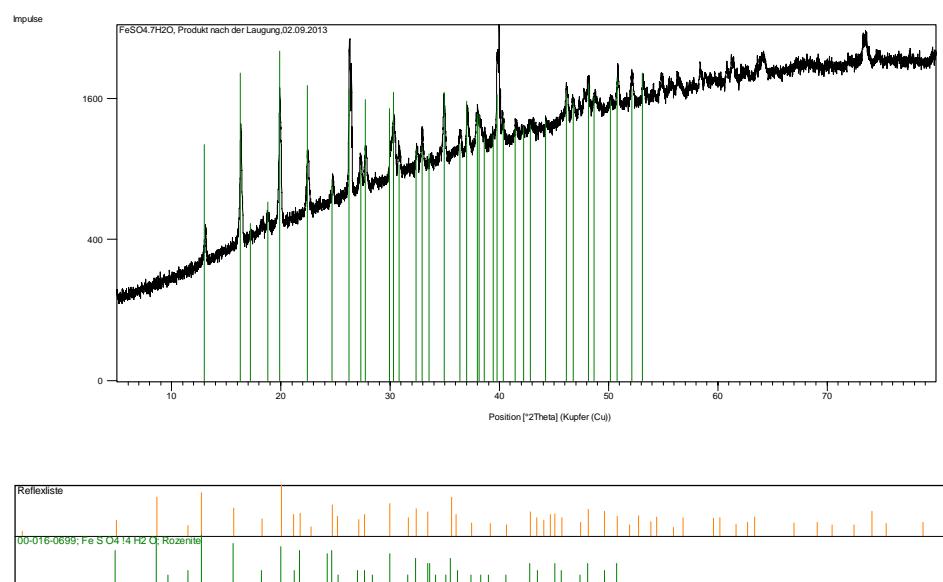


Fig. 11. X-ray diffraction pattern of the produced copperas

Process evaluation

As already mentioned in the introduction, none of the investigations that are known from the literature on the leaching of ilmenites upon mechanical activation have led to any kind of technical applicability [30-38]. In different mills, milling times of up to 200 hours were required and, with one exception, the solids content for the leaching process was only 10 g/l [35]. The operating parameters are summarised in table 2. Hydrolysis products were gained in only two cases [32, 36].

The operating conditions determined in this investigation fulfil the requirements for a technical implementation of the process for the production of a synthetic TiO₂ product, which is suitable for use in aluminothermic alloy production. **Figure 12** shows the process flow chart on the coupling of hydrometallurgical processing of ilmenites into synthetic TiO₂ concentrate (anatase) with the aluminothermic production of TiAl alloys.

Table 2: Operating parameters from the literature on the mechanical activation of ilmenite for direct leaching with H₂SO₄.

Bibliography	Mill	t [h]	H ₂ SO ₄ [%]	c [g/l]	T [°C]	T _L [h]	m [%]	Product
Welham, N., Llewellyn, N.J., (1998), [30]	Vertical ball mill	0.25 - 100	50	10	up to 120	0.5 - 8	Ti: 90	solution
Chen, Y. et al. (1999), [31]	Vertical ball mill, in air and vacuum	10 - 200	50	10	100	2	Ti: 100 (vacuum) Ti: 70 (air)	solution
Li, Ch. et al. (2008), [32]	Vertical ball mill	4	5, 10, 15	10	100	0.25 - 4	Ti: 85 Fe: 100 (0.25 h) TiO ₂ (95%) rutile Fe ₂ O ₃ (0.5%) SO ₃ (4.1%)	TiO ₂ (95%) rutile Fe ₂ O ₃ (0.5%) SO ₃ (4.1%)
Li, Ch. et al. (2006), [33]	Planetary ball mill	0.5 - 10	50	10	up to 100	0.25 - 2	Ti: 82	solution
Sasikumar, C. et al. (2004), [34]	Planetary ball mill	0.5; 1.5; 4	50	10	up to 120	0.5 - 4	Ti: 65 Fe: 90	solution
Sasikumar, C. et al. (2007), [35]	Planetary ball mill	0.5; 1.5; 4	16-75	111-167	up to 120	0.5 - 4	Ti: 40 Fe: 78	solution
Li, Ch. et al. (2007), [36]	Ball mill in air and vacuum	2, 4, 6, 10	5, 10, 20	10	up to 100	0.25 - 4	Ti: 90 Fe: 90 (0.5 h) TiO ₂ rutile Fe ₂ (TiO ₃) ₃ pseudorutile	TiO ₂ rutile Fe ₂ (TiO ₃) ₃ pseudorutile
Li, Ch. et al. (2006), [38]	Vertical ball mill simultaneous milling and leaching (attritor)	0.5 - 4	50	26	up to 120	0.5 - 4	Ti: 77	solution

t – milling time; c – solids content; T_L – leaching time; m - recovery

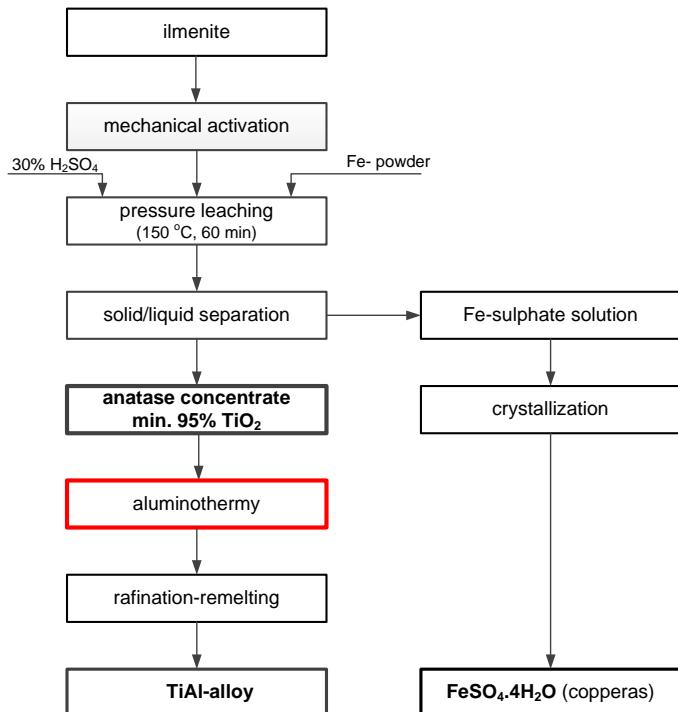


Fig. 12. Process flow chart on the coupling of hydrometallurgical processing of ilmenites with the aluminothermic production of TiAl alloys.

The energy required per tonne of synthetic anatase is expected to be 506 kWh. Based on current costs for energy, this corresponds to approx. 212 euro per tonne of synthetic anatase. The use of untreated ilmenite in aluminothermic processes would result in the production of ferrotitanium. The reduction of by-components in ilmenite is more favourable than the reduction of titanium dioxide because of their lower oxygen affinity. This investigated pretreatment of ilmenite with mechanical activation and leaching enables new cost-effective production methods for titanium based alloys. Due to the increase of TiO₂ content up to 95% the usage of synthetic anatase in aluminothermic reaction is feasible and attractive [47]. So far, only high purity rutile pigments have been used for the aluminothermic production of TiAl alloys [48-50]. The potential reduction reactions of by-components have specific enthalpies that must be taken into account for the thermochemical calculations of the aluminothermic reaction mixture. The effect of grain size and morphology on the aluminothermic process is not predictable and has to be investigated in-depth. At 95% TiO₂, the synthetic TiO₂ concentrate (anatase) that we produced meets the requirements for aluminothermy in order to produce Titanium based alloys instead of Ferro-based alloys from ilmenite.

Summary

The reaction kinetic conditions for the processing of mechanically activated ilmenite by means of direct hydrometallurgical conversion in autoclave to synthetic

anatase at 150°C with 30% H₂SO₄ were investigated and the parameters for technical implementation determined. Based on the found operating data, a process flow chart on the coupling of the hydrometallurgical processing of mechanically activated ilmenite into synthetic anatase with the aluminothermic production of TiAl alloy products was established.

For the first time ever, this concept supplies a suitable TiO₂ raw material for aluminothermic processes in order to produce Titanium alloys from ore concentrates by means of direct hydrometallurgical processing of ilmenites after mechanical activation.

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References

- [1] Produktionsintegrierter Umweltschutz bei der Aufbereitung und Aufarbeitung von Rohstoffen. In: Handbuch des Umweltschutzes und den Umweltschutztechnik, Band 2, Springer Verlag, Berlin-Heidelberg-New York 1996, ISBN 3-540-58059-X.
- [2] Noda, T.: Titanium from Slag in Japan, *Journal of Metals*, 17, 1965, (1), 25-32.
- [3] Meyer, K., Pietsch, H. Marine Seifenlagerstätten, eine Basis für interessante Industrieprojekte, Titanoxid und seine Herstellung, *Erzmetall* 27, 1974, 345-350.
- [4] Lee, H.Y., Poggi, D.: Mine, Mill and Smelting Complex at Richards Bay, South Africa, *The Metallurgical Society of CIM, Annual Volume*, 1978, 93-96.
- [5] Watanable, M., Sei, R., 1988. Method for recovering titanium. European Patent 0,198,763-A2.
- [6] Roche, E.G., Stuart, A.D., Grazier, P.E., 2004. Production of Titania. WO2004035841-A1.
- [7] Roche E.G., Stuart, A.D., Grazier, P.E., Nicholson, S., 2005. Production of Titania. WO2005038060-A1
- [8] Stuart, A.D., Reynolds, G.A., Lawson, J.A., 2005. Production of titania. WO Patent 2005090619-A1.
- [9] Stuart, A.D., Lawson, J.A., Ward, C.B., Peng, H., 2010. A sulphate process. WO Patent 2010034083-A1.
- [10] Berkovich, S.A., 1975. Recovery of Titanium from Ores. US Patent, 3903239.
- [11] Duyvesteyn, W., Sabachy, B., Verhulst, D., Edmund, V., West-sells, P.G., 2001a. Processing titaniferous ore to titanium dioxide pigment, WO Patent 2001/00531 A1.
- [12] Duyvesteyn, W., Sabachy, B., Edmund, V., Verhulst, D., West-sells, P.G., Spitler, T.M., Vince, A., Burkholder, J.R., Paulus, B.J., Huls, M., 2002. Processing titaniferous ore to titanium dioxide pigment, US Patent 2002/6375923 B1.
- [13] Verhulst, D., Sabachy, B., Spitler, T.M., Duyvesteyn, W., 2002. The Altair TiO₂ pigment process and its extension into the field of nanomaterials. *CIM Bulletin ProQuest Science Journals* 95 (1065), 89-94.
- [14] Verhulst, D., Sabachy, B., Spitler, T., Prochazka, J., 2003. New developments in the Altair hydrochloride TiO₂ pigment process. *Hydrometallurgy* 2003, 5th

- International Conference in Honor of professor Ritchie, Vancouver, August 2003, vol. 1, pp. 565-575.
- [15] Liu, Y.M., Qi, T., Chu, J.L., Tong, Q., Zhang, Y., 2006. Decomposition of ilmenite by concentrated KOH solution under atmospheric pressure. International J. Mineral processing 81, 79-84.
 - [16] Qi, T., Liu, Y.M., Chu, J.L., Li, H.J., Li, Z.H., 2005. Preparation of potassium titanate using sub-molten salt method. China patent, CN 200510059715.5.
 - [17] Tong, Q.J., Qi, T., Liu, Y.M., 2007. Preparation of potassium titanate whiskers and titanium dioxide from titaniferous slag using KOH sub-molten salt method. ChineseJ. Process Engineering 7 (1), 85–89.
 - [18] Xue, T., Wang, L., Qi, T., Chu, J., Qu, J., Liu, C., 2009. Decomposition kinetics of titanium slag in sodium hydroxide system. Hydrometallurgy 95, 22–27.
 - [19] Thomas, J.B., 1985. Titanium dioxide pigment production from Ilmenite. European Patent 0186370.
 - [20] Girgin, I., Turker, L., 1986: Hydrochloric acid leaching of Ilmenite-effect of alcohol species, AusIMM Bull. Proc. 291, 61-64.
 - [21] Lakshmanan, V. I., Sridhar, R., Rishea, M. M., and Joseph, D. E. Laat R, 2001. Production of titanium metal from titanium-bearing ores involves leaching and selective removal of iron values by solvent extraction. US Patent 2001/007646–A1.
 - [22] Lakshmanan, V. I. and Sridhar, R., 2002. Methods for separation of titanium from ore, Canadian patent 2289967.
 - [23] Lakshmanan, V.I., Sridhar, R., Hains, D.H., 2004a. A novel hydrometallurgical process for very high purity TiO₂ production. Proceedings of 17th Industrial Minerals International Congress. Cambrian Printer, Aberystwyth, UK, pp. 92–95.
 - [24] Lakshmanan, V. I., Sridhar, R., Rishea, M. M., and Joseph, D. E. Laat R., 2004b. Methods for separation of titanium from ore. U.S. patent 2004/6699446–B2.
 - [25] Lakshmanan, V. I., Sridhar, R., Harris, B. G. and Puvvada, G., 2005a. Process for the recovery of titanium in mixed chloride media. WO patent 2005/049872.
 - [26] Lakshmanan, V. I., Sridhar, R., Harris, B. G. and Puvvada, G., 2005b. Process for the recovery of titanium in mixed chloride media. US patent 2005/0142051 A1. Lakhsman und Sridhar, 2002.
 - [27] Puvvada, G.V.K., Sridhar, R., Lakshmanan, V.I., 2003. Chloride metallurgy: PGM recovery and titanium dioxide production. JOM 38–41.
 - [28] Zhang, Y., Qi, T., Zhang, Y., 2009. A novel preparation of titanium dioxide from titanium slag. Hydrometallurgy 96, 52–56.
 - [29] Gock, E.: Beitrag zur mechanischen Aktivierung von Titanomagnetit. Dissertation TU-Berlin, 1968.
 - [30] Welham, N., Llewellyn, N.J.: Mechanical enhancement of dissolution of ilmenite. Minerals Engineering 11 (1988) 827-841.
 - [31] Chen, Y., Williams, J.S., Campbell, S.J., Wang, G.M.: Increased dissolution of ilmenite induced by high-energy ball milling. Materials Science and Engineering A271 (1999) 485-490.
 - [32] Li, Ch., 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 115 (2008) 293-300.

- [33] Li, Ch., Liang, B., Guo, L., Wu, Z.: Effect of mechanical activation on the dissolution of Panzhihua ilmenite. *Minerals Engineering* 19 (2006) 1430-1438.
- [34] Sasikumar, C., Rao, D.S., Srikanth, S., Ravikumar, B., Mukhopadhyay, N.K., Mehrotra, S.P.: Effect of mechanical activation on the kinetics of sulphuric acid leaching of beach sand ilmenite from Orissa, India. *Hydrometallurgy* 75 (2004) 189-204.
- [35] Sasikumar, C., Rao, D.S., Srikanth, S., Mukhopadhyay, N.K., Mehrotra, S.P.: Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H₂SO₄. *Hydrometallurgy* 88 (2007) 154-169.
- [36] Li, Ch., Liang, B., Guo, L.: Dissolution of mechanically activated Panzhihua ilmenites in dilute solutions of sulphuric acid. *Hydrometallurgy* 89 (2007) 1-10.
- [37] Tao, T., Glushenkov, A.M., Chen, Q., Hu, H., Zhou, D., Zhang, H., Boese, M., Liu, S., Amal, R., Chen, Y.: Porous TiO₂ with a controllable bimodal pore size distribution from natural ilmenite. *Cryst. Eng. Comm.* 13 (2011) 1322-1327.
- [38] Li, Ch., Liang, B., Chen, S.: Combined milling-dissolution of Panzhihua ilmenite in sulfuric acid. *Hydrometallurgy* 82 (2006) 93-99.
- [39] Boldyrev, V.V. und Meyer, K.: *Festkörperchemie*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1973.
- [40] Juhasz, A.Z., Opoczky, L.: *Mechanical Activation of Minerals by Grinding*. Ellis Horwood Limited, Chichester, 1990.
- [41] Baláž, P.: *Extractive Metallurgy of Activated Minerals*, Elsevier, Amsterdam, 2000.
- [42] Gock, E., Vogt, V., Kähler, J.: *Winnacker, Küchler Chemische Technik*, Band 6a, 5. Auflage Seite 158 ff. Wiley-VCH Verlag GmbH & Co. KGaA 2006
- [43] Gock, E.: Erzeugung von synthetischem Anatas aus Ilmeniten mit Dünnsäure. Offenlegungsschrift DE 3635010 A1. 10/10/1986
- [44] Gock, E., Kurrer, K.-E.: Eccentric Vibratory Mill: Industrial introduction of a new construction series, Proceedings of the XX IMPC – Aachen, 21.-26. September 1997, pp. 267-276.
- [45] Kurrer, K.-E., Gock, E.: *Powder Technology* 105, Elsevier-Verlag, 1999, S. 302-310.
- [46] Gock, E., Corell, J.: „Schwingmühlen“ im Verlag BHM Springer Wien New York, 151. Jg. (2006), Heft 6
- [47] Hassan-Pour, S.: DFG Forschergruppe 1372/Titan, Teilprojekt 3 Pyrometallurgische Gewinnung von kostengünstigen Titanwerkstoffen durch kinetisch kontrollierte Feststoff-Aluminothermie und anschließende Raffination im Elektroschlackeumschmelzprozess, 2013
- [48] Hammerschmidt, J.: Entwicklung einer Prozessroute zur Herstellung von γ -TiAl-Legierungen durch Aluminothermie und Schutzgas-Elektroschlackeumschmelzen, D82 (Diss. RWTH Aachen) Shaker Verlag, ISBN 3-8322-1971-4, Aachen 2003
- [49] Stoephasius, J.-C., Friedrich, B.: Modelling of metallothermic reactions local reaction rates during aluminothermic γ -TiAl-Nb production. *World of Metallurgy-Erzmetall A*, Vol. 58(2) (2005) 63-69
- [50] Stoephasius, J.-C.: Elektroschlackeraffination aluminothermisch hergestellter Titanaluminide; Schriftenreihe des IME, Band 14, 2006, Shaker Verlag Aachen, ISBN 978-3-8322-5876-4