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Titanium Recovery from Aluminium and Titanium Dioxide Production Residues

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Abstract

The Horizon project EURO-Titan aims upscaling Ti-oxide, metal and alloy powder manufacturing from metallurgical residues, abundantly available in Europe. The demonstration of the overall process is planned at the “Alumina” Ltd. Zvornik, an alumina plant (Bosnia-Herzegovina) and at ORANO (France). For Ti extraction from bauxite residues (BR), reduction at 1600°C in an electric arc furnace and magnetic separation removed most of the iron. In this study we will represent hydrogen reduction of aluminium and titanium residues at 920°C using hydrogen in rotary kiln. Previously, the EAF Ti-enriched slag leaching experiments by sulfuric acid at variable pressure obtained highest yield of titanium oxysulphate with Ti-leaching efficiency (95%) at 150 °C using 5 mol/L sulfuric acid at 9 bar oxygen in 2 h. In this work we will explain the leaching behaviour of solid residue obtained in the absence of smelting conditions at 1600°C. For TiO_2-pigment production residues from sulphate processing, Ti-leaching by sulphuric acid through gave lower leaching efficiency under high pressure in an autoclave, as some Ti-compounds could not be dissolved. Submicron TiO_2-powders were prepared from Ti oxysulphate, using ultrasonic spray pyrolysis with hydrogen reduction between 700 and 1350°C.

Introduction

Titanium, thanks to its light weight, high corrosion resistance and alloying capacity, is used widely in medical, aerospace, construction sectors, and technologies related to energy sectors ([1] *and papers therein*).

Titanium alloy manufacturing through Powder Metallurgy (PM) has the advantage to produce a wide variety of alloys, to maximize material use, to achieve complex or tailored shapes, near-net-shape dimensional control. It is cost efficient at moderate- to high-volume component production [2]. Ti-alloys’ mechanical properties produced by PM are competitive to wrought Ti-alloys. Therefore, Titanium alloy Powder Metallurgy (PM) is gradually growing in (bio-) medical, structural and aerospace applications.

The preparation of titanium bearing powders is the first step prior to blending, compacting, sintering sizing/impregnation or secondary operations [1].
The Horizon project EU Titan (N°101135077, www.euro-titan.eu) aims to upscale and combine eco-friendly processing steps to extracting and recycling titanium in Europe, with a focus on minimizing its carbon footprint and promoting sustainability through industrial symbiosis. Utilizing processing waste as feed materials, bauxite residue (BR) and white pigment production residues our consortium will manufacture titanium in the form of metal powder to reduce Europe’s import dependency.

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This paper presents first results on the quality of Titanium powders such as titanium oxide using ultrasonic spray analysis, what is only one part of the general EURO-TITAN strategy, as shown at Figure 1.

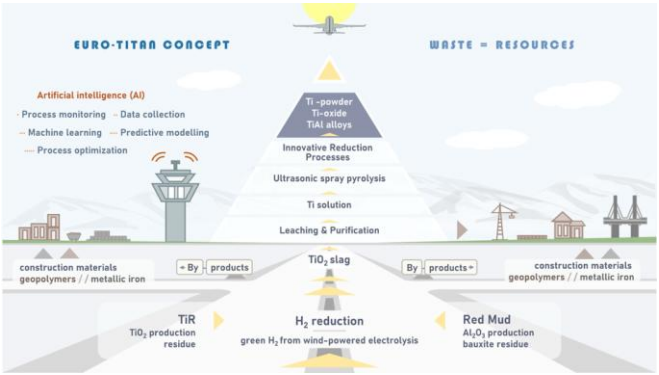

Figure 1. EURO Titan's concept of turning metallurgical residues into valuable products

EXPERIMENTAL

Materials

In this work, Bauxite residues ("red mud") from the factory "Alumina" Ltd. Zvornik was used as a raw material from the aluminium industry. BR was dried, grounded, and prepared for the reduction process. The chemical composition of the used BR is shown Table 1.

Table 1: Composition of bauxite residue from "Alumina" Ltd. Zvornik, Rep. Serbia.

Compounds	Wt., %	Compounds	Wt., %
Ignition loss at 1000° C	8.32	Ga_2O_3	0.225
SiO_2	10.52	CuO	0.007
Fe_2O_3	49.29	K_2O	0.159
Na_2O	2.45	Tl_2O_3	0.088
TiO_2	4.59	MnO	0.145
CaO	8.23	MgO	0.627
Al_2O_3	12.03	NiO	0.034
Ag_2O	0.001	PbO	0.019
BaO	0.014	P_2O_5	0.930
Cr_2O_3	0.133	ZnO	0.016
Sc_2O_3	0.011	V_2O_5	0.135
Co_2O_3	0.012	SrO	0.075

BR characterization was performed using Inductive Coupled Plasma Spectroscopy (ICP-OES) and Electron Diffraction Spectroscopy (EDS) analysis (Table 1). X-Ray Diffraction (XRD) analysis [3] of BR has confirmed the presence of hematite and other stable oxides to reduction, including ilmenite. The analysis also shows other non-ferrous minerals, such as perovskite, calcite, diaspore, boehmite, anhydrite, which are main part of bauxite residues.

The company Venator, Duisburg, Germany has delivered two titanium dioxide residue samples from the production of titanium dioxide using "sulphate" process (Table 2).

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Table 2: Chemical composition of titanium residues from Venator, Duisburg, Germany.

Sample	Al_2O_3	TiO_2	SiO_2	Na_2O	CaO	MgO	K_2O	Cr_2O_3	Fe_2O_3
UA	3.92	60.6	17.2	0.33	1.90	2.26	0.22	0.08	8.59
H	3.03	46.6	17.3	0.66	0.53	0.98	0.51	0.56	0.54

The main components of sample UA, that contains mixed 50 % slag and 50 % ilmenite, are composed of rutile (TiO_2), Magnesium titanium oxide ($(Mg_{0,9}Ti_{2,1})O_5$), and kennedyite ($(Fe_{0,33}TiO_{0,46}Mg_{0,21})(Ti_{1,9}Mg_{0,1})O_5$). Therefore, the content of titanium oxide is about 60%, and the extraction of titanium is a challenge for the future work. The main components of sample H are armalkolite ($MgTi_2O_5$), ilmenite ($FeTiO_3$), and quarz (SiO_2). The TiO_2 content is very high (46.6 %). Treatment of aluminium and titanium residue contains combined pyrometallurgical and hydrometallurgical treatment.
In this paper titanium recovery from bauxite and titanium dioxide production residues (UA) will be describing aiming the formation of titanium oxide.

Methods

The pyrometallurgical treatment of BR was previously performed in static conditions such as reduction using plasma hydrogen [3] and carbothermic reduction [4] in an electric arc furnace and direct hydrogen reduction in small tubular furnace [5]. To improve the mixing process the reduction of BR with hydrogen was performed in dynamic conditions using rotary kiln Carbolite, Germany (Figure 2).

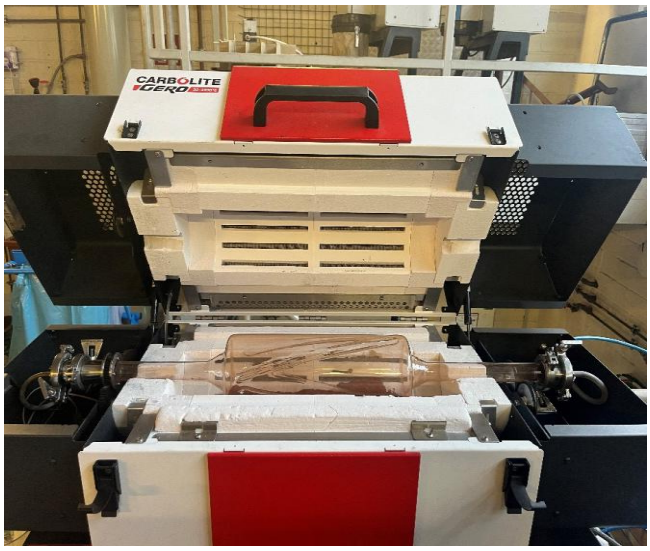

Figure 2. Rotary kiln for hydrogen reduction

The used parameters for hydrogen reduction are as follows: initial mass of sample: 200 g, temperature: 920°C, Atmosphere: hydrogen and nitrogen; Flow rate: 1-2 L/min. Before hydrogen reduction, nitrogen was used to evacuate oxygen from a cylindrical quartz tube situated in a rotary kiln, checking for leakage in the system. Bubblers with demineralized water was used to check the continuous gas flow in the system. Nitrogen was continuously supplied during heating. After successful BR reduction, magnetic phases were separated from solid residues. Hydrogen reduction was performed below the iron melting point. Physical separation was employed to isolate magnetic from non-magnetic phases.

Valuable metals were extracted from reduced slag using sulfuric acid treatment. Key leaching parameters, including the solid-to-liquid ratio, pressure, and acid concentration, were maintained constant throughout the experiments. Variables such as temperature, reaction time, stirring speed, and particle size were optimized based on insights from prior experimental work. A 5 M sulfuric acid

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solution was prepared in a 1-liter flask and introduced into a Buchi autoclave, containing solid residue derived from the hydrogen reduction from rotary kiln (Figure 3).

The system was pressurized to 9 bars with oxygen, the temperature was set to the desired level, and the magnetic stirrer was operated at a speed of 500 rpm. The leaching process, in a Buchi autoclave, was conducted up to 120 minutes.The leaching process was performed, Switzerland, a specialized system designed for acid leaching with a capacity of 1.53 L, a maximum pressure of 200 bar, and a maximum temperature of 270 °C, and 2000 rpm. The autoclave is equipped with a heat exchanger controlled by a thermostat, a mixer, pressure adjustment probes, and the capability for sample extraction during operation. The system is fully integrated with computer software, enabling precise control and real-time monitoring of operational parameters, with all data recorded for detailed post-experiment analysis. The pressure within the system was monitored using both a manometer and digital sensors, with the total pressure comprising oxygen (9 bar) and water vapor (12–15 bar). Cooling was achieved using a dedicated cooling system, and the heating rate was controlled at 10 °C/min.

Figure 3. Picture of the high pressure autoclave.

Prior to each run, the autoclave was manually sealed with screws and subjected to a pressure integrity test to ensure safe and reliable operation. After the leaching process was completed, the autoclave was cooled to room temperature, and the system pressure was carefully released. The leachate solution was then subjected to filtration and neutralization with distilled water. Filtration was conducted using a vacuum-assisted filtration system integrated into the setup, ensuring effective separation of solid and liquid phases.

Final step in our work is the synthesis of titanium oxide from titanium oxysulphate using ultrasonic spray pyrolysis and hydrogen. Ultrasonic spray pyrolysis with hydrogen reduction is used for the

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synthesis of titanium-based powders from the titanium oxysulphate ($TiOSO_4$ VENATOR Hombityl UN 3264, Duisburg). The innovation of this study is testing of an industrial solution of $TiOSO_4$ for the synthesis of nanosized TiO_2. This was presented in our previous work [6]. For the experiments, industrial titanium oxysulphate was used with 1 M concentration, purity 99.9%, density 1.361 g/cm^3. The ultrasonic generator, PRIZNANO, Kragujevac, Serbia was used to produce aerosol. Process parameters which have been observed are temperature, concentration of the precursor, and different hydrogen: argon ratio at the constant frequency of 1.7 MHz. The hydrogen and argon flow rates were controlled by flowmeter and then mixed before entering US generator. The synthesis was performed between 700 and 1300°C using ultrasonic spray pyrolysis equipment (Figure 4).

Figure 4. Scheme of USP equipment a) Gas flow regulation; (b) ultrasonic aerosol generator; (c) furnace with the wall-heated reactor; (d) collection bottles.

Results and Discussion

The obtained results after hydrogen reduction of BR in rotary kiln and leaching of the solid residues are shown in Table 3.

Table 3: Chemical composition of the solution after leaching in an autoclave (200 °C, 5 mol/L H_2SO_4 and s/L (1:10)); 12 bar; 4h)

Concentration (g/l)	Fe	Ti	Al	Si
UA without reduction	6.59	1.16 (8.4 %)	0.58	0.017
Reduced UA	8.31	2.14 (12.6 %)	0.73	0.049
Reduced bauxite residue	24.4	2.29 (98.8 %)	3.66	0.066

Our results confirm the high leaching efficiency of titanium from previously reduced red mud in contrast to the tionite UA under same conditions. The reason for this very low solubility of UA is because of rutile phase remains highly stable, resisting complete dissolution even under intensified conditions. The influence of particle size of UA-particles was analyzed for different fraction: < 63µm; 63-125µm¸125-230µm and >230µm in the absence of reduction. The obtained results are presented in Table 4:

Table 4: Chemical composition of the solution after leaching in an autoclave (150°C, 5mol/L H_2SO_4 and s/L (1:10)); 9 bar; 2h)

Concentration of UA (g/L), no reduction	Fe	Ti	Al
<63µm	2.12	2.66 (14.10)	0.21
63-125 µm	2.03	2.03 (10.76)	0.19
125-230 µm	2.41	2.90 (15.37)	0.19
>230µm	2.84	3.08 (16.32)	0.23

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These results confirm a maximum titanium leaching efficiency of 16.32%. Rutile resists to the applied leaching conditions and remains undissolved. Larger particle sizes of rutile exhibit higher leaching efficiency, suggesting that preferentially smaller particles of rutile remain undisolved.

The maximal leaching efficiency of titanium amounts 98.8 % from previously reduced bauxite residues with hydrogen in dinamic conditions, what confirms our previous results obtained using carbothermic reduction at 1600°C [7]. XRD Analysis of initial BR and reduced BR in rotary kiln has shown the changes in structure of solid residue (Figure 5a,b).

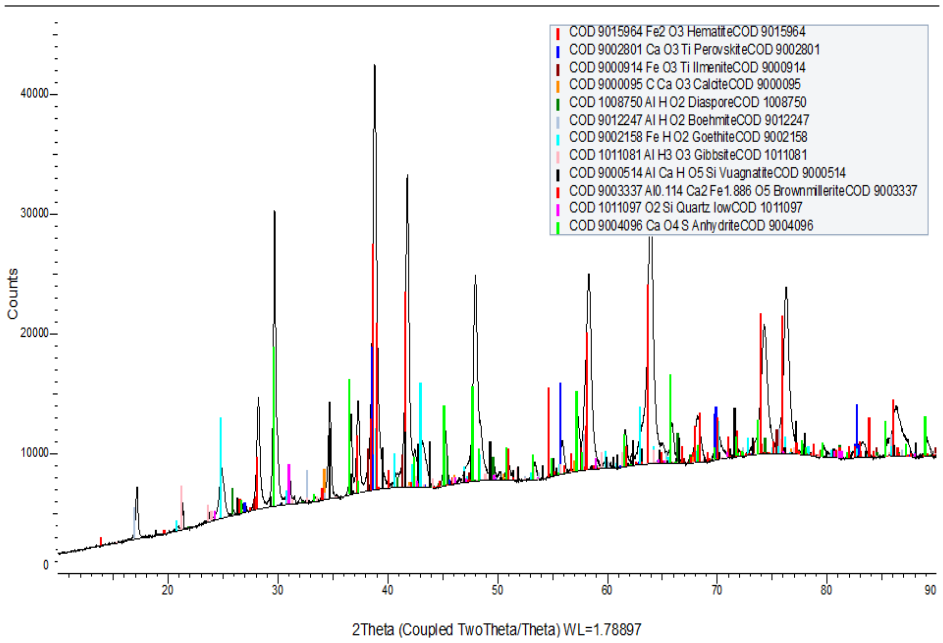

Figure 5a. XRD of BR before hydrogen reduction at 920°C

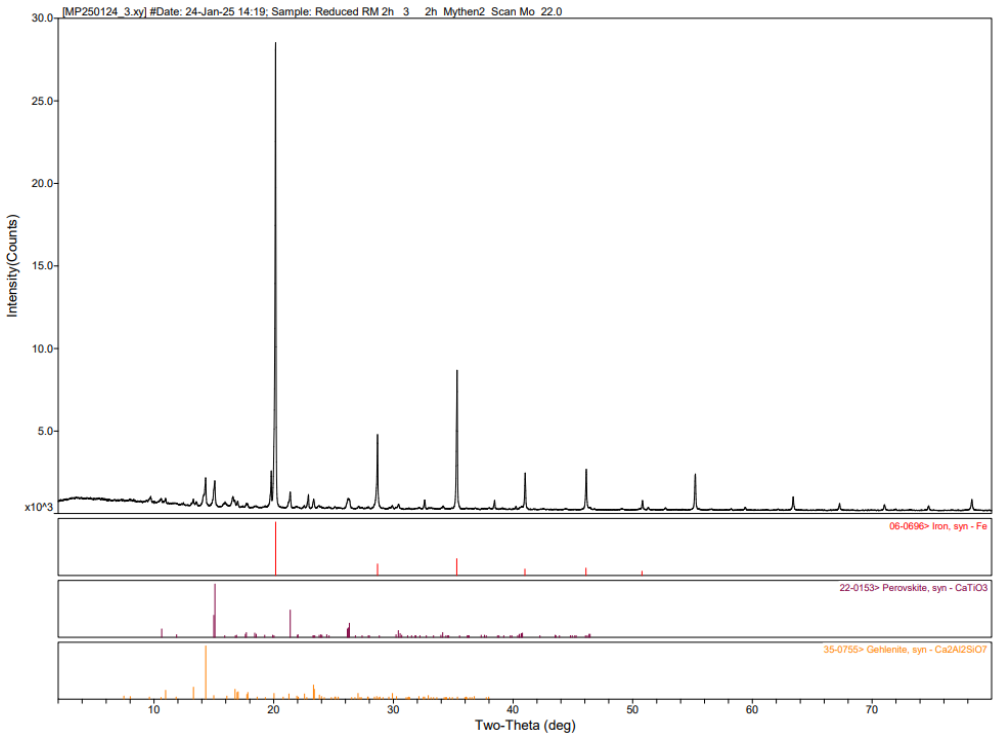

Figure 5b. XRD of BR after hydrogen reduction in rotary kiln at 920°C

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Identified phases in solid residue after hydrogen reduction in rotary kiln are iron, perovskite, and gehlenite (Figure 5b). Hematite (main phase in BR, Figure 5a) was successfully reduced with hydrogen in rotary kiln at 920°C. Formation of perovskite and gehlenite confirms structural modifications. This reduction demonstrates the potential of hydrogen reduction in altering BR composition without smelting process opening possibilities for valuable material recovery from BR.

After purification of solution obtained by reduction process and high pressure in autoclave, the formation of $TiOSO_4$ is needed for ultrasonic spray pyrolysis. Formation of nanosized submicron particles of Titanium oxides from his solution using ultrasonic spray pyrolysis in hydrogen atmosphere is confirmed at Figure 6 between 700°C and 1350°C.

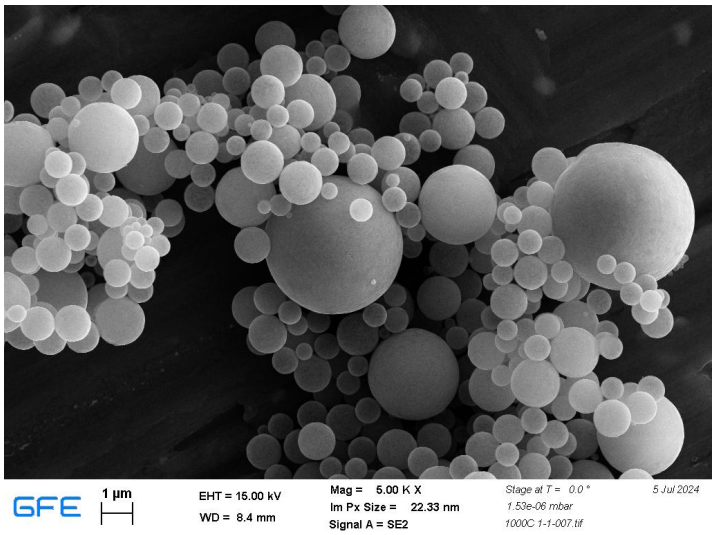

Figure 6. Typical particles of titanium oxide obtained at 700°C using ultrasonic spray pyrolysis.

The obtained particles are ideally spherical with nano-and submicron size.

Conclusions

The combined strategy of EURO-TITAN project containing reduction of BR and titanium dioxide production residues (tionite UA) with ultrasonic spray pyrolysis in hydrogen atmosphere leads to formation of submicron and nanosized titanium oxide. The leaching efficiency of titanium from red mud after hydrogen reduction in rotary kiln at 920°C amounts 98.8 % in contrast to treatment of UA tionite. Complex mineralogical structure is reason for this different behaviour between aluminium and titanium residues. The following steps will be performed to destroy the mineralogical structure of tionite to prepare solid residue for leaching process. The main aim and challenge of this work are production of metallic titanium during molten salt electrolysis and titanium aluminium vanadium alloys using aluminothermic reduction.

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References
[1] Manne, P., K., Kumar, N., S., Lakshmi, A.A., Subbiah, R. (2020). Powder Metallurgy for Titanium Alloys-a Review. E3S Web of Conferences 184, 01045, https://doi.org/10.1051/e3sconf/202018401045

[2] Wang, Z., Tan, Y., Li, N. (2023). Powder metallurgy of titanium alloys: a brief review. Journal of alloys and compounds, 965, 171030, https://doi.org/10.1016/j.jallcom.2023.171030

[3] Stopic, S., Schneider, R., Kostić, D., R. Souza Filho, I., Perusic, M., Emil-Kaya, E., Bernd Friedrich, B., Combined decarbonizing technologies for treatment of bauxite residues, Waste, 2025

[4] Stopic, S., Kostic, D., Emil-Kaya, E., Uysal, E., Gürmen, S., Mitrašinovic, A., Perušic, M, Friedrich, B, High-Pressure and High-Temperature Dissolution of Titanium from Titanium and Aluminum

 https://doi.org/10.59499/EP256759760

Residues: A Comparative Study, Surfaces 2024, 7, 1096–1108. https://doi.org/10.3390/surfaces7040072

[5] Srecko Stopić,, Nenad Nikolić, Dragana životić, Jugoslav Krstić, Milena Rosić, Vladimir Damjanović, Bernd Friedrich Hydrogen Metallurgy for a treatment of bauxite residues-First results on the EURO-TITAN Project, Proceeding, Plenary Lecture, 1-11, XXV Yucorr Conference, Divcibare, 2024

[6] Kostic, D., Stopic, S., Keutmann, M., Emil-Kaya, E., Volkov-Husovic, T., Perušic, M., Friedrich, B. Synthesis of Titanium-Based Powders from Titanium Oxy-Sulfate Using Ultrasonic Spray Pyrolysis, Materials 2024, 17, 4779. https://doi.org/10.3390/ma17194779

[7] Stopic, S, Kostic, D, Schneider, R , Sievers, M., Wegmann, F., Emil Kaya, E., Perušic, M., Friedrich, B. Recovery of Titanium from Red Mud Using Carbothermic Reduction and High Pressure Leaching of the Slag in an Autoclave. Minerals 2024, 14, 1151. https://doi.org/10.3390/min14111151

 https://doi.org/10.59499/EP256759760