BR06 - Ferrotitanium Production from BR: A Study of the Aluminothermic Process

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Abstract

Titanium oxide is a major component of bauxite residue with a high value, but it is often an unwanted element in common BR reuse options such as cement or iron production. Conventional carbothermic reduction smelting of BR produces a slag still containing a large amount of Ti. This study investigates an aluminothermic process for producing a FeTi alloy by combining BR, ilmenite ore, and fluxes. Based on thermodynamic calculations and batch experiments, the aluminum (reductant) and the fluxes amounts were investigated to achieve the optimum alloy production in parallel with a slag that could be further valorized in the cement industry. The mineralogical and chemical analysis of the metallic and slag phase agreed with the thermodynamic calculations. The results obtained by this study can lead to developing a new process for the complete valorization of BR and paving the way for scaling up aluminothermic processes for producing ferroalloys from all iron-rich residues.

Keywords: Aluminothermic, Ferrotitanium, Bauxite Residue

1. Introduction

Bauxite residue, also known as red mud, is a byproduct generated during the processing of bauxite ore to extract alumina, the primary raw material used in aluminum production. When bauxite is processed using the Bayer process, alumina is separated from the ore, leaving behind a highly alkaline and fine-grained residue known as bauxite residue.

Bauxite residue management is a significant concern for the aluminum industry due to its environmental impact. If not properly managed, bauxite residue can pose challenges related to alkalinity, trace metal leaching, and its potential for embankment failures [1]. Various approaches are being explored to find sustainable solutions, including recycling and using bauxite residue in building materials and soil improvement [2-3]. Understanding the composition of bauxite residue and the role of its containing oxides is crucial for developing effective strategies for its safe and environmentally responsible management.

The composition of bauxite residue varies depending on the source of the bauxite ore and the specific processing methods employed. Generally, bauxite residue consists of several major components, with the most significant ones being metallic oxides and hydroxides like iron, titanium, aluminum, silicon, calcium and sodium [4]. These compounds, in particular, play a crucial role in determining the properties and potential environmental impacts of the bauxite residue. Titanium is one of the significant impurities found in bauxite residue, although its presence can vary depending on the source of the bauxite ore and the processing methods used. Titanium is commonly present in bauxite residue in the form of titanium oxides, such as rutile and anatase (TiO_2), cancrinite ($CaTiO_3$) and ilmenite ($FeTiO3$) [4]. For the recovery of Ti from

BR, numerous studies have been made, primarily by looking at hydrometallurgical processes [5-7]. Due to its high reactive nature, extraction of titanium metal directly from TiO_2 is very difficult. However, since it forms a solid solution with iron, thus reducing its own activity, its extraction via the formation of a FeTi alloy can be deemed possible.

Ferrotitanium is commonly used as an additive in the steelmaking industry to enhance the characteristics of steel. The addition of ferrotitanium to steel can have several effects, including deoxidation, strengthening, grain refinement and corrosion resistance [8-9]. Ferrotitanium comes in different grades and compositions, typically ranging from around 30 to 75 wt% titanium content. The specific composition of ferrotitanium used in steelmaking depends on the particular application and the desired properties of the final steel product.

In this present work, BR and ilmenite where mixed and evaluated the possibility to produce ferrotitanium via the aluminothermic route.

2. Materials

BR, used in this work was obtained from MYTILINEOS S.A.-Aluminium of Greece, Ag. Nikolaos, Greece. The chemical composition of this BR consisted mainly of Fe_2O_3: 38.10%, TiO_2: 5,00%, SiO_2: 7.82%, Al_2O_3: 23.28%, CaO: 8.37%, Na_2O: 3.15% wt. The ilmenite used for this study had a chemical composition of Fe_2O_3: 32.41%, TiO_2: 60.09 % wt. Other raw materials used included aluminium powder (>91% Al), CaO powder (>98% CaO), and $NaClO_3$ (>99%).

3. Theoretical Calculation

The main reactions taking place in this process are the reductions of the iron and titanium oxides by the aluminium powder as shown in the following equations:

$$3FeO + 2Al \rightarrow 3Fe + Al_2O_3$$
$$3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3$$
$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

$NaClO_3$ is an exothermal agent that reacts in order to provide more heat to ensure that the reaction takes place spontaneously and auto-thermally, and that the temperatures created during this exothermic reaction are higher than the melting point of the slag created. CaO was introduced as a slag forming agent since it forms a low-temperature complex oxide with Al and helps with the viscosity of the slag.

Thermodynamic analysis was implemented with the use of the thermodynamic commercial software FACTSAGE 8.2® [10]. The equilibrium module was used to predict thermodynamically the evolution and composition of the phases under varying temperature and composition conditions. A mixture of 50% wt BR and 50%wt Ilmenite was assumed with varying degrees of metallic aluminium and lime additions at 1650 °C. To evaluate the effect of Al additions, (Figure 1) in a mix without lime, addition of up to 10% excess in stoichiometric Al is proposed in order to avoid the precipitation of solid phases from the slag (which would result in a highly viscus melt). It is also evident that the more aluminium added to the system the more liquid metal is formed but with increasing Al content, which means that any excess of Al will not react any further.

The Al additions were fixed to 10% stoichiometric excess and adding 10-20 wt.% CaO into the mix (Figure 2), it is observed to extend the liquid area and reduce the melting point. Higher lime additions will result in formation of a perovskite solid solution, which is a high temperature phase and will precipitate out of the slag thus making the viscosity high.

The calculated composition of the alloy to be produced for a 50% BR-50% Ilmenite raw material mix and 15%wt lime addition is shown in Figure 3.

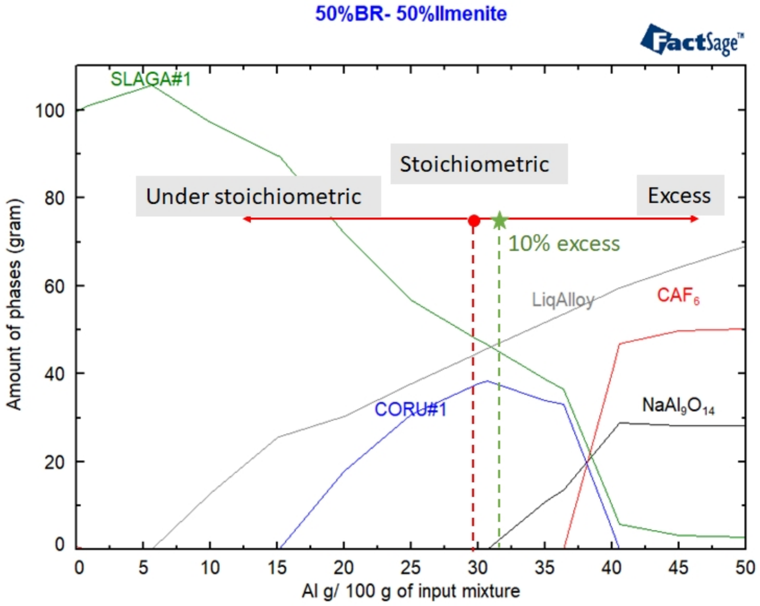

Figure 1: Equilibrium calculation results for the phases present at 1650 °C starting from 50-50 mix of BR and ilmenite for varying amounts of Al metal addition. SLAGA#1 stands for a liquid slag phase, CORU#1 for $(Al,Cr,Fe,Mn)_2O_3$ and CAF6 for $Ca(Al, Fe)_{12}O_{19}$ solid solutions.

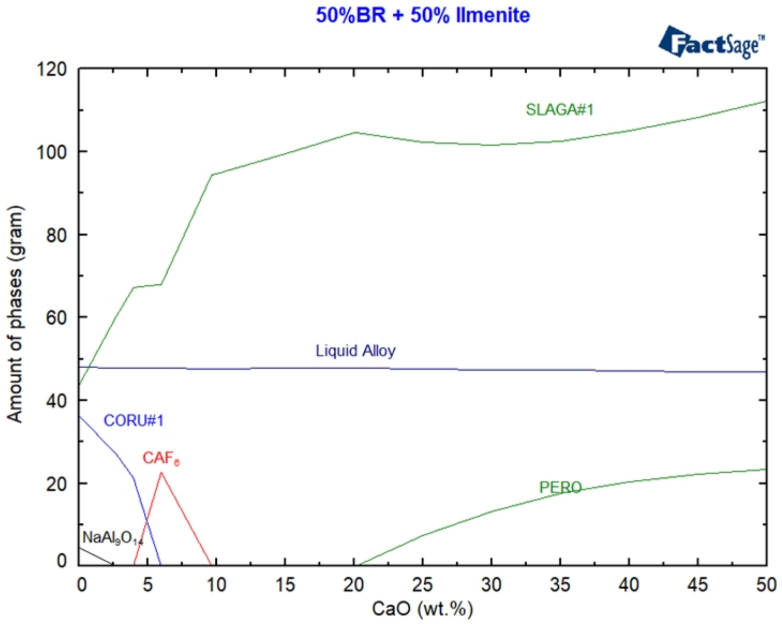

Figure 2: Equilibrium calculation results for the phases present at 1650 °C starting from 50-50 mix of BR and ilmenite at 10% excess Al addition and for varying amounts of CaO addition. SLAGA#1 stands for a liquid slag phase, CORU#1 for $(Al,Cr,Fe,Mn)_2O_3$, CAF6 for $Ca(Al, Fe)_{12}O_{19}$ and PERO for $Ca_2Ti_2O_6 – Ca_2Ti_2O_5$ solid solutions.

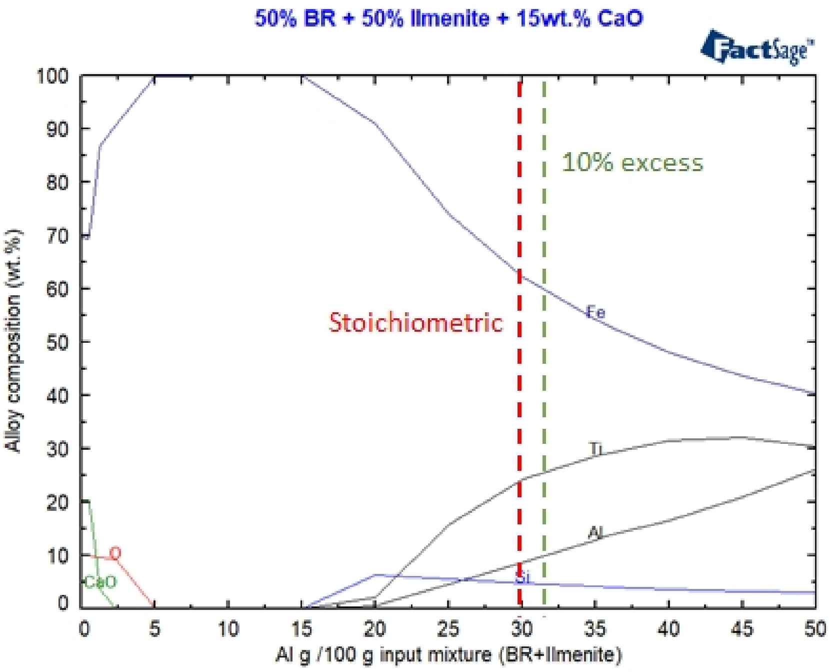

Figure 3: Equilibrium calculation results for the alloy composition at 1650 °C starting from 50-50 mix of BR and ilmenite and a 15 %wt lime addition with varying amounts of Al addition.

4. Experimental Methods

BR, Ilmenite and CaO powder were dried in an oven at 105 °C for 24 h. The raw materials ratios variated from 80 %BR- 20 % Ilmenite to 50 % BR-50 % Ilmenite. Using only BR would lead to an alloy with very low Ti content, thus lower than the standards from ISO 5454-1980 [11]. Also, the use of only ilmenite is well established as a process. $NaClO_3$ was added 20 wt % relative to the weight of TiO_2 contained in the raw materials mix. Aluminium powder was added in a 10% excess than stoichiometrically needed. The compositions were mixed and then inserted in a graphite crucible inside an induction furnace under an Argon atmosphere (Figure 4, Left). The exothermic reaction was initiated by providing a small amount of power to the furnace and then it was self-sustained. After cooling to room temperature, the alloy was separated from the slag (Figure 4, Right).

5. Results

The chemical composition of the ferrotitanium produced is presented in Table 1. As it was expected the more ilmenite was contained in the mix the higher the Ti content in the alloy. The Si and Al content was elevated as well, a result of the presence of Si in the BR and the excess of Al as a reducing agent.

Table 1. Chemical Composition of FeTi alloy produced.

BR/Ilmenite (%/%)	Fe (%)	Ti (%)	Si (%)	Al (%)
80/20	67.35	24.24	7.46	2.84
70/30	63.36	27.36	6.78	3.47
60/40	59.35	31.32	5.93	4.34
50/50	54.01	35.82	5.04	5.47

Figure 4. Left: Induction Furnace used in experiments; Right: Ferrotitanium alloy produced.

The slag produced in this process had a high alumina content, and a TiO_2 concentration from 2 to 2.5%, as seen in table 2.

Table 2. Chemical compositions of the slags produced.

BR/Ilmenite (%/%)	Al_2O_3	CaO	Na_2O	SiO_2	Fe_2O_3	TiO_2
80/20	69.45	10.76	4.37	2.51	2.13	1.93
70/30	68.12	10.18	4.12	2.27	2.81	2.37
60/40	68.73	11.35	4.83	2.38	2.58	2.11
50/50	70.2	12.24	5.04	2.12	3.47	2.51

6. Discussion

The resulting alloys compared to the thermodynamic predictions are relatively close. In the 50/50 mix the FactSage model predicted about 10 percentile points less Ti in the alloy (26.4 %), in favour of more Al (10.3 %) and Fe (58.78 %). Given that final equilibrium calculation depends on the set temperature of 1650 °C, this deviation is to be expected.

The alloy produced from the 50/50 mix meets the standards set by the ISO 5454-1980 as a FeTi40Al8 alloy. However, complete transformation of the Ti oxides to a metallic phase was not possible. An explanation is the formation of TiO during the reduction of TiO_2. TiO is a basic oxide capable of creating compounds with alumina, thus staying in the slag phase. The calcium aluminate slag can be used for Al extraction [12] or used as raw material for calcium aluminate cements, leading to a zero-waste process.

A possible optimization to the process can happen with the use of other bauxite residues with a higher Ti content, thus reducing the need of virgin Ilmenite in the mix. The use of Fe-Ti slags instead of Ilmenite can also be considered. Finally impure aluminium scrap or aluminium drosses can be used as the reducing agent, introducing more circularity in the process. While such an approach could help valorize unused metallic aluminium secondary resources, it could also pollute the final alloy with unwanted metals.

7. Conclusions

The use of BR as an iron and titanium source in the aluminothermic production of FeTi alloys has been proven on the laboratory scale. BR has been combined with ilmenite and reduced autothermically with metallic aluminium powder. Lime and $NaClO_3$ were added as fluxes to the process to reduce the melting point of the slag and sustain an autothermic reaction. When a 50/50 BR – ilmenite raw mix was used a commercial FeTi alloy was produced. These results can offer a new scope to the production of ferrotitanium alloys and to the valorization of Bauxite Residue.

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