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Communication

Thermodynamics of Aluminothermic Processes for Ferrotitanium Alloy Production from Bauxite Residue and Ilmenite

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Abstract: Titanium oxide is a major component of bauxite residue (BR) 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 an FeTi alloy by combining BR, ilmenite ore, and fluxes. Based on thermodynamic calculations and batch experiments, the amounts of aluminum (reductant) and fluxes 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 the development of a new process for the complete valorization of BR, paving the way for scaling up aluminothermic processes for producing ferroalloys from all iron-rich residues.

Keywords: aluminothermic; ferrotitanium; bauxite residue

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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 most 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 ($FeTiO_3$) [4]. For the recovery of Ti from BR, numerous studies have been carried out, primarily by looking at hydrometallurgical processes [5–7]. Due to its highly reactive nature, extraction of titanium metal directly from TiO_2 is very difficult. However, since it forms a solid solution with iron, its extraction via the formation of an FeTi alloy may be possible [8].

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 [9,10]. Ferrotitanium comes in different grades and compositions, typically ranging from around 30% to 75% titanium content. The specific composition of ferrotitanium used in steelmaking depends on the application and the desired properties of the final steel product.

In the present work, BR and ilmenite were mixed, and the possibility of producing ferrotitanium via the aluminothermic route was evaluated. The aluminothermic method for producing FeTi from ilmenite has been the most widely used in recent years. Ilmenite is mixed with Al and other fluxes inside a hearth or an electric furnace, and this highly exothermic reaction produces an FeTi alloy and high-alumina slag [8].

2. Materials

The 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%, and Na_2O: 3.15%. The ilmenite used for this study had a chemical composition of Fe_2O_3: 32.41% and TiO_2: 60.09%. The other raw materials used included aluminum powder (>91% Al), CaO powder (>98% CaO), and $NaClO_3$ (>99%).

3. Theoretical Calculations

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

$$3FeO + 2Al \rightarrow 3Fe + Al_2O_3$$

$$3TiO_2 + 4Al \rightarrow 3Ti + 2Al_2O_3$$

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

Thermodynamic analysis was implemented with the use of the thermodynamic commercial software FACTSAGE 8.2® [11]. The equilibrium module was used to thermodynamically predict the evolution and composition of the phases under varying temperatures and metallic Al additions. A 50%-50%wt BR–Ilmenite mixture was initially considered as the raw material. The amount of Al needed to transform iron and titanium oxides from this mixture into metals based on the above equations is hereafter referenced as the stoichiometric Al requirement.

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. The CaO additions should be sufficient for the slag-making reactions, assuming stoichiometric Al, thus keeping the resulting oxides in a liquid state (slag) without precipitating high-temperature solids or solid solutions, as shown in Figure 1.

The aluminothermic reaction is exothermic, and the adiabatic temperature changes due to the reaction are presented in Figure 2b. As expected, the adiabatic temperature increases with increases in the Al content in the input mixture. A temperature of 1650 °C was arbitrarily selected to implement the calculations, as at this temperature, liquid slag and alloy will be the dominant phases (Figure 2c).

Figure 2 presents the results for a mixture of 50%-50%wt BR and ilmenite and 12 wt.% CaO (according to Figure 1) at 1650 °C. Increasing the additions of Al for 100 g of input mixture results in increasing amounts of liquid alloy, whereas that of liquid slag decreases due to the precipitation of high-temperature phases.

The more Al added, the higher the amount of the liquid alloy produced, as mentioned (Figure 2a). At very high additions of Al, the Ti content starts to decrease, whereas that of Al increases, which implies that the resulting alloy will be outside of the desired range as specified earlier, Figure 2d. Fe_2O_3 reduces first from the slag, as was expected according to its thermodynamic affinity towards the alloy's formation. TiO_2 reduces partially to Ti_2O_3 and Ti, whereas the former reduced Ti-oxide remains in the slag, even with high Al contents. In addition, more Al metal will promote the reduction of Si, as can be seen from the reduction in SiO_2 and the increase in Si in the slag and metal, respectively (see Figure 2e).

The amount of Ti in the alloy produced is calculated to be app. 26 wt.% for 10% excess from the stoichiometric Al and around 12% CaO addition as a fluxing agent (Figure 2d). However, increasing the BR content of the input mixture at 80% BR–20% ilmenite reduces the amount of Ti that can be obtained in the alloy to about 20% and increases the demand of Al, as shown in Figure 2f. As such, the amount of Al should be controlled to optimized values which clearly depend on the TiO_2 content of the input materials.

According to the aforementioned analysis and optimization, the four different raw material mixtures of BR and ilmenite (Table 1) were considered. In each case, the respective 10% excess of stoichiometric Al was added at 1650 °C. The results of the thermodynamic calculations for the produced metal and slag phases are presented in Tables 1 and 2, respectively. These results were used as a guide for the experimental design and the resulting observations that will be discussed in the subsequent sections.

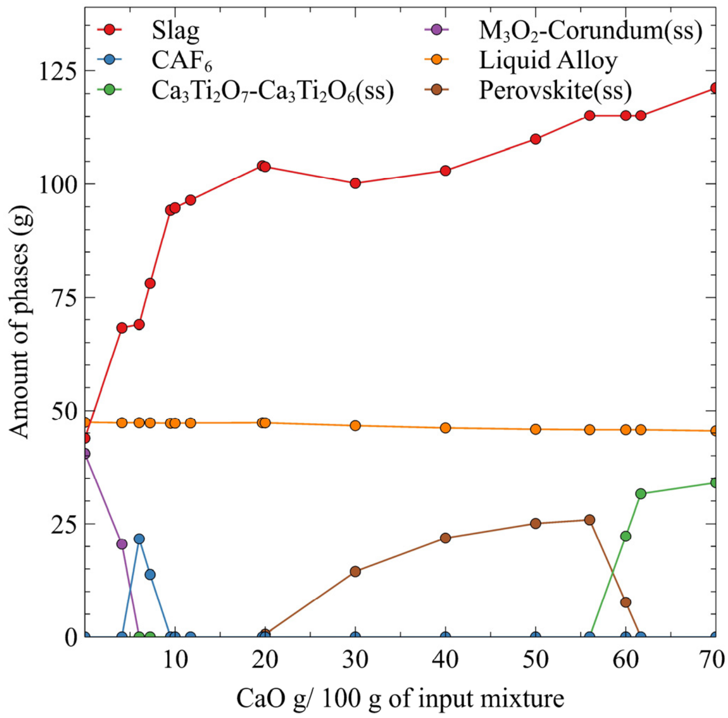

Figure 1. Effect of CaO additions in 100 g of input BR and Ilmenite (50%-50%), assuming stoichiometric Al at 1650 °C.

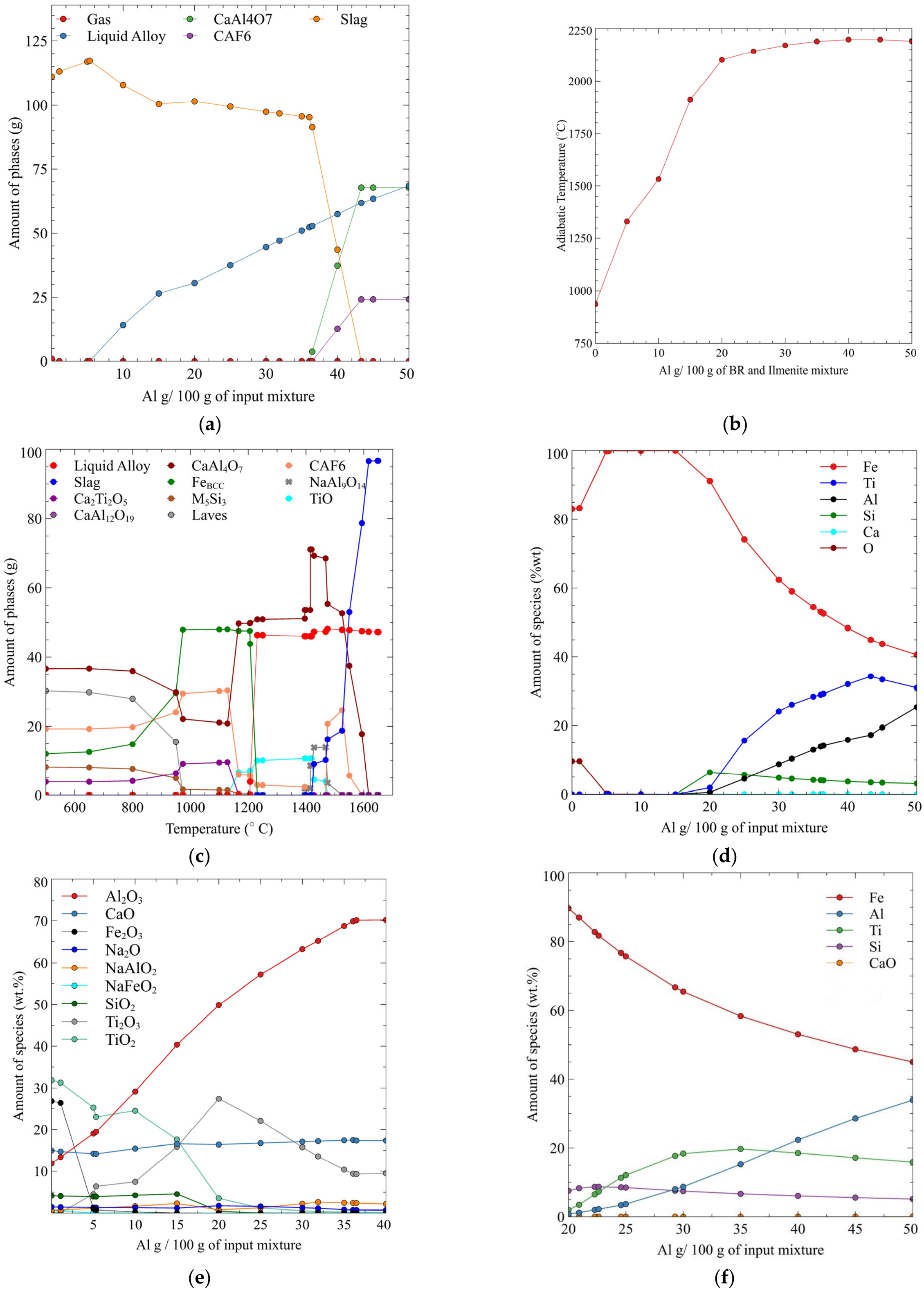

Figure 2. Thermodynamic predictions of the effect of the 50–50 mixture on (**a**) the phase assemblage with increased Al contents; (**b**) the adiabatic temperature as a function of Al additions; (**c**) the phase evolution for 10% excess Al at varying temperatures; (**d**) the composition of alloy with varying Al inputs; (**e**) the composition of slag with varying Al inputs. (**f**) The composition of alloy in an 80%–20% mixture with varying Al contents. CAF6 stands for Ca(Al, Fe)$_{12}$O$_{19}$; CAF2 for Ca(Al, Fe)$_4$O; NCA2 for Na$_2$(Na$_2$, Ca)Al$_4$O$_8$; and Laves for Fe$_2$Ti, M$_5$Si$_3$ for Ti$_5$Si$_3$ solid solutions.

Table 1. Calculated chemical composition of FeTi alloy.

BR/Ilmenite (%wt/%wt)	Fe (%wt)	Ti (%wt)	Al (%wt)	Si (%wt)
80/20	76.5	11.5	3.6	8.6
70/30	69.6	17.3	6	7
60/40	63.7	22.2	8.3	5.8
50/50	58.9	26.2	10.5	4.4

Table 2. Calculated chemical composition of the slag phase.

BR/Ilmenite (%wt/%wt)	Al_2O_3 (%wt)	CaO (%wt)	Na_2O (%wt)	SiO_2 (%wt)	TiO_2 (%wt)	Ti_2O_3 (%wt)
80/20	65.5	22.4	2.8	0.2	0.6	8.6
70/30	67.8	19.1	2.4	-	0.4	10.3
60/40	67.6	18.2	2.1	-	0.4	11.7
50/50	66.9	17.2	2.	-	0.4	13.4

4. Experimental Method

Ilmenite and CaO powder were dried in an oven at 105 °C for 24 h. The raw material 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, being thus lower than the standards from ISO 5454-1980 [12]. Additionally, the use of only ilmenite is well established as a process. $NaClO_3$ was added at 20 wt.% relative to the weight of TiO_2 contained in the raw material mix. NaClO3 is an exothermal agent that reacts in order to provide more heat to ensure that the reaction takes place spontaneously/autothermally and that the temperatures created during this exothermic reaction are higher than the melting point of the slag created.

Aluminum powder was added in a 10% excess over what was stoichiometrically needed. The compositions were mixed and then inserted into a graphite crucible inside an induction furnace under an argon atmosphere (Figure 3a). 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 3b). The alloy and the slag were analyzed in AAS after a dissolution with aqua regia and $LiBO_4$ fusion, respectively.

(**a**) (**b**)

Figure 3. (**a**) Induction furnace used in experiments; (**b**) ferrotitanium alloy produced.

5. Results

The chemical composition of the ferrotitanium produced is presented in Table 3. As was expected, the more Ilmenite was contained in the mix, the higher the Ti content in the alloy. The Si and Al contents were also elevated a result of the presence of Si in the BR and the excess of Al as a reducing agent. 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 4.

Table 3. Chemical composition of FeTi alloy.

BR/Ilmenite (%wt/%wt)	Fe (wt.%)	Ti (wt.%)	Si (wt.%)	Al (wt.%)
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

Table 4. Chemical composition of the slag phase.

BR/Ilmenite (%wt/%wt)	Al_2O_3 (%wt)	CaO (%wt)	Na_2O (%wt)	SiO_2 (%wt)	Fe_2O_3 (%wt)	TiO_2 (%wt)
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

Mixtures of BR and ilmenite have been considered in the present study, and several mixing ratios of the raw materials have been evaluated in both the theoretical and experimental parts of the work. A higher fraction of ilmenite in the feed mixture caused an increase in the Ti content of the final alloy, as estimated from the thermochemical simulations (Table 1), in agreement with the experimental trends (Table 3). More ilmenite in the feed mixture introduces more Ti into the system (according to mass balance calculations), and more Al is required for the reduction reactions, therefore promoting the introduction of more Ti and Al in the alloy phase. For all the alloys, the Ti content varies between 12–27 wt.%; Al and Si have maximum contents of 10 wt.% and 8 wt.%, respectively. The 50–50 (BR/ilmenite) mixture can be anticipated in an alloy with a composition close to ISO specifications (for FeTi40Al8), according to the experimental observations. In addition, it can be found that an increase in added Al results in increased Ti, Al, and Si contents in the alloy (Figure 2), suggesting that the increase in Al promotes the reduction of Si and Ti oxides. Noticeably, when the amount of Al was increased to approximately 30 wt.% (for 100 g of total mixture mass), the increasing trend of the Ti content in the alloy was reduced, and that of Al continuously increased, implying that the alloy will be richer in Al. The reduction sequence of the oxides from the slag with Al as reducing agent was found feature Fe_2O_3 first, whereas TiO_2 and SiO_2 were close with respect to their reduction course. The thermochemical results can provide evidence of the mechanism of TiO_2 reduction in forming slag. The liquid alloy forms from Al additions of approximately 5 wt.% and higher; the amount of Ti in the alloy is insignificant for additions of Al up to approximately 15 wt.%, which implies that Ti is first reduced to Ti_2O_3 and then reduces further to Ti. TiO_2 is partially reduced to Ti_2O_3 in the slag, which is a stable oxide, with higher Al additions. The amount of Al_2O_3 increases in the slag with increased Al additions; however, the amount of Al_2O_3 between the slags from the various mixtures (Table 2) is not significantly different, and varies between 65.5 and 68 wt.%. The Si content in the alloys according to equilibrium calculations is consistent with the experimental observations (Tables 1 and 3). Nevertheless, the estimated and measured compositions (Tables 1 and 3) are not intended for direct comparison as the estimated compositions are derived from calculations at 1650 °C, whereas in the experiments, the local temperature could differ as a result of the exothermic reactions. The adiabatic temperature calculations indicate that when the amount of Al was increased to approximately 30 wt.%, and the adiabatic temperature could be as high as 2170.5 °C (Figure 2). Furthermore, calculations were implemented at the adiabatic temperature (Figure 4). The estimated composition of slag and metal at 1650 °C, however, seemed to better match the experimental results.

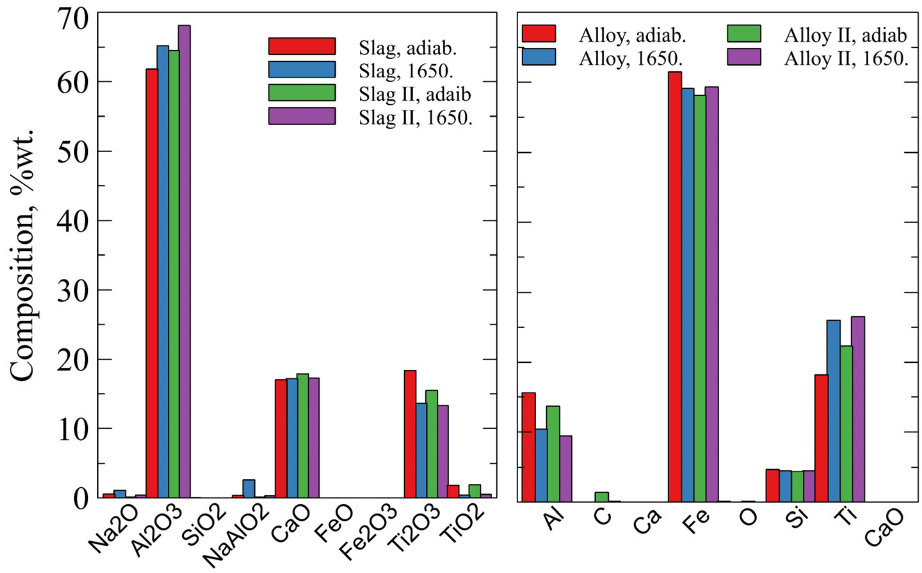

Figure 4. Composition of slags (**left-hand side**) and metals (**right-hand side**) at 1650 °C and at the adiabatic temperature with and without (II) assumed carbon solubility, as estimated with FactSage 8.2.

Finally, some solubility of C has been assumed in the alloy, which could be introduced in the melt from the refractory materials, and the results are projected in Figure 4. Slag and alloy signify the results without carbon additions, whereas slag II and alloy II are at carbon saturation conditions. The Al content in the alloy is found to increase at adiabatic temperature, whereas that of Ti reduced. When C has been assumed, the Al and Ti contents reduce slightly, which implies that C will not significantly affect the predicted composition. The temperature seems to have a more pronounced influence on the predicted compositions. Although the compositions of alloys and slags between the experiments and the simulations differ to some extent, it is still believed that the simulations can provide evidence on the reaction mechanisms and give a fair estimation of the general trends, also considering deviation from equilibrium conditions and experimental and analytical errors. It is further suggested that the suitability of the developed datasets should be examined further against the experimental compositional and temperature ranges. The used database has been developed for systems which could deviate from the present system and as such introduce uncertainties in the calculations. Further work should be focused on the compatibility of the datasets with the compositional ranges to provide even more accurate thermodynamic descriptions for ternary and higher-order systems.

Experimentally, the alloy produced from the 50–50 mix meets the standards set by ISO 5454-1980 as an FeTi40Al8 alloy. The calcium aluminate slag can be used for Al extraction [13] or used as a raw material for calcium aluminate cement, leading to a zero-waste process.

Possible optimization of the process can happen with the use of other bauxite residues with a higher Ti content, thus reducing the need for virgin ilmenite in the mix. The use of Fe-Ti slags instead of ilmenite can also be considered. Finally, impure aluminum scrap or aluminum dross can be used as a reducing agent, introducing more circularity in the process. While such an approach could help valorize unused metallic aluminum 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 was combined with ilmenite and reduced autothermically with metallic aluminum powder. Lime and $NaClO_3$ were added to the process as fluxes 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 perspective on the production of ferrotitanium alloys and on the valorization of bauxite residue.

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Data Availability Statement: The data presented in this study are available within the article.

Conflicts of Interest: Author Efthymios Balomenos was employed by the company Mytilineos SA. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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