A novel dense Al₂O₃-Ti₂O₃ slag synthesized while ferro-titanium alloy making
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ABSTRACT
This paper describes the preparation route and formation mechanism of a Al₂O₃–Ti₂O₃ composite. During the fabrication of a ferro-titanium alloy from titanium concentrate via a thermit method, CaO is generally added to reduce the viscosity of the liquid and promote the separation of the ferro-titanium alloy and Al₂O₃–CaO–TiO₂ slag. The latter represents a multi-oxide system mainly composed of CaAl₂O₄, CaAl₂O₇, and CaTiO₃ species with poor high-temperature performance, which considerably limits its practical application. The performance optimization and high value-added application of this slag involve the elimination of the CaO phase and replacement of TiO₂ with Ti₂O₃ particles to prevent the formation of a multi-oxide system due to the low solubility of Ti₂O₃ in Al₂O₃. The Al₂O₃–Ti₂O₃ composite material was successfully prepared via industrial experiments, and its synthesis mechanism and corresponding reaction model are established.

1. Introduction
The abundance of titanium ranks fourth among metals, lower than iron, aluminum, and magnesium. According to the data released by the United States Geological Survey (USGS) in 2021, ilmenite accounts for about 90% of the world’s consumption of titanium minerals. World anatase, ilmenite and rutile resources total over 2 billion tons. And the ferro-titanium alloy produced from ilmenite is an additive to produce high-strength structural steel and special steel [1–4]. Industrial production of ferro-titanium alloy is commonly obtained by the cost-effective thermit reduction method [5–8]. The slag composed of CaAl₂O₄ (CA6), CaAl₂O₇ (CA2), perovskite and a little corundum. It has low melting temperature and poor high-temperature performance. Currently, only a small amount is used in bauxite-based refractory castables. The efficient use of this waste slag is a problem to be solved urgently.

The effective way to completely solve the efficient use of the slag is to eliminate the CaO. Without CaO, the composition of the slag will be composed of Al₂O₃ and titanium compounds, which can improve the high-temperature performance of the slag, and the valence of titanium can be controlled. In production process, the presence of titanium is a key factor for realization of the process. If titanium exists in the form of titanium dioxide, aluminum titanate will be formed, and the slag composition will be mainly aluminum titanate and corundum [9,10]. It is expected that the titanium can be adjusted to TiO₂ₓ(0 < x < 2), and the composition will be corundum and TiO₂ₓ complex phase [11,12].

The paper proposes a new process to produce ferro-titanium alloy, which can produce ferro-titanium alloy and at the same time obtain a slag material with high added value. The material has broad application prospects for the following reasons. (1) It exhibits the corundum-like high-temperature properties and, therefore, can be used as a refractory material. (2) Dispersing Ti₂O₃ among corundum grains can increase their toughness to produce an ideal abrasive material [13]. (3) The presence of titanium compounds can be controlled through process optimization. While the reaction Ti₂O₃ + O₂ + Al₂O₃ → TiO₂ + Al₂O₃ occurs in an oxidizing atmosphere, the TiC/TiN/TiCN corundum-based composite material is formed in a reducing atmosphere [14]. (4) The Al₂O₃–Ti₂O₃ composite is easy to obtain and environmentally friendly; furthermore, it increases the utilization rate of natural resources.

1.1. Experimental
In this study, a titanium concentrate (TiO₂ ≥ 40 wt%, Fe₂O₃ ≥ 30 wt%, CaO≤2 wt%, MgO≤2 wt %, Al₂O₃ ≤ 2 wt %, MnO≤1 wt %,0–1 mm) was used as the raw material, and metallic Al powder (Al₂O₃ ≥ 98 wt%, ≤45 μm, add 40 wt % of titanium concentrate) served as the reductant. Titanium concentrate was preheated at about 500℃, then mixed with Al powder evenly. The mixed powder was sprinkled into the reaction bag, and the reaction time was about 15 minutes. Before the adjustment, CaO (CaO≥99 wt%) was added to the reaction mixture to form a phase with a low melting point (such as calcium aluminates), which reduced the viscosity of the liquid and promoted the separation of
the alloy and slag. After the adjustment, the upper layer is the slag, and lower layer is the ferro-titanium alloy as shown in Figure 1(a).

The slag material before the improvement is shown in Figure 1(b), and the slag obtained after the modification as shown in Figure 1(c). The elemental composition of the prepared by-produced was determined by X-ray fluorescence spectrometry (Arl Perform X, Thermo Fisher), while its phase analysis was performed via X-ray diffraction (XRD; Ultima IV, Rigaku, CuKα) in the scanning range of 10–90°. The microstructure and elemental distribution of the composite specimen were obtained through scanning electron microscopy (SEM; Quanta FEG450, FEI, 20KV) combined with energy-dispersive spectrometry. Samples for the elemental distribution analysis were sectioned from the prepared materials, polished, and coated with gold. Their apparent porosity and density were measured via the ISO 5017 standard method.

2. Results and discussions

2.1. Experimental data

The chemical compositions and select physical properties of the raw materials are listed in Table 1. The main components of sample before modification are Al₂O₃, CaO, and TiO₂. The main components of sample after modification are Al₂O₃ and TiO₂. The titanium content in sample after modification is higher than sample

![Figure 2](image)

**Figure 2.** XRD patterns recorded for various materials. (a) XRD pattern of sample after modification. (b) XRD pattern of before modification. (c) XRD pattern of ferrotitanium alloy.

|             | Bulk density (g/cm³) | Apparent porosity (%) | Al₂O₃ (%) | TiO₂ (%) | SiO₂ (%) | Fe₂O₃ (%) | CaO (%) | MgO (%) | K₂O (%) | Na₂O (%) | ZrO₂ (%) |
|-------------|---------------------|-----------------------|-----------|----------|----------|-----------|---------|---------|---------|----------|----------|
| Before mod. | 3.11                | 9.3                   | 74.67     | 13.37    | 0.27     | 0.11      | 9.91    | 1.40    | 0.03    | 0.06     | 0.18     |
| After mod.  | 3.63                | 10.1                  | 72.31     | 23.19    | 0.46     | 0.12      | 0.79    | 2.49    | 0.03    | 0.12     | 0.49     |

*X-ray fluorescence spectrometry presents Ti as TiO₂ only.
before modification; these samples have low impurity contents. The bulk density of sample after modification is higher than that of sample before modification.

The XRD patterns of the studied samples are shown in Figure 2. Sample before modification consists of the CaAl₃O₇Ca(OH)₀.₆₋₀.₄ (CA6) (PDF#38-0470), Al₂O₃ (PDF#83-2080), CaAl₂O₄ (CA2) (PDF#76-0706), and CaTiO₃ (PDF#42-0423) phases. Sample after modification is mainly composed of the Al₃O₃ (PDF#74-1081) and Ti₂O₃ (PDF#71-1055) phases, Al₂TiO₅ (PDF#73-1630), and MgAl₂O₄ (PDF#75-1796) species were also detected. Finally, Fe₂TiO₅ (PDF#65-0602) is the main phase of the ferrotitanium alloy with the inclusion of some TiO₂ (PDF#12-0754) and Al₁₁Fe₄ (PDF#47-1420) species.

Figure 3(a and b) displays the SEM images of sample before modification. The gray areas correspond to the calcium aluminate phase, and the white areas denote titanium-containing compounds (CaTiO₃) that are finely and uniformly dispersed in the specimen matrix.

Figure 4(a–c) shows the SEM images of sample after modification. Figure 4(a) depicts its overall appearance, wherein the white area denotes the titanium-containing compound, and the gray area represents corundum species (note that corundum and Ti₂O₃ are two separated phases, and Ti₂O₃ particles are distributed across the corundum phase). In Figure 4(b), the bright white area corresponds to the Ti₂O₃ phase, the light white area denotes the Al₂TiO₅ phase, and the inset shows the titanium element surface scan. Finally, Figure 4(c) shows the distribution of Ti₂O₃ particles in the specimen pores.

These results indicate that after the process is adjusted, the expected Al₂O₃–Ti₂O₃ composite material, consisting of the separate Ti₂O₃ and Al₂O₃ phases, is successfully obtained.

2.2. Ti₂O₃–Al₂O₃ composites assessment

The following reactions occur in the process of reducing TiO₂ with Al:

\[ n\text{TiO}_2 + 2/3\text{Al} = \text{Ti}_n\text{O}_{2n-1} + 1/3\text{Al}_2\text{O}_3 \] (1)
\[ \text{TiO}_2 + 1/3\text{Al} = 1/2\text{Ti}_2\text{O}_3 + 1/6\text{Al}_2\text{O}_3 \] (2)
\[ \text{TiO}_2 + 2/3\text{Al} = \text{TiO} + 1/3\text{Al}_2\text{O}_3 \] (3)
\[ \text{TiO}_2 + 4/3\text{Al} = \text{Ti} + 2/3\text{Al}_2\text{O}_3 \] (4)

The observed reduction sequence is TiO₂ → TiₙO₂ₙ₋₁ (n = 4–10) → Ti₃O₅ → Ti₂O₃ → TiO → Ti [15]. Ti₃O₅ (n = 4–10) compounds are called the Magnéli phase, which represents a series of continuous titanium compounds with oxygen content ranging from 63.6% to 65.5% [16,17]. Ti₃O₅ and Ti₂O₃ are black titanium oxides, which are preferentially obtained during the Ti reduction process. Ti₃O₅ is produced at a high temperature and low oxygen partial pressure; otherwise, the Ti₃O₅ phase is formed. TiO is a low-valent titanium oxide with a face-centered cubic structure containing a relatively high number of vacancies at the metal and oxygen lattice sites (approximately 15%). Relationship of \( P_{\text{O}_2} / P^0 \) and T for the phases is shown in Figure 5. The purpose of smelting is to reduce all titanium oxides to titanium; the excessive reductant creates a liquid reaction environment with

![Figure 3](image1.png)

**Figure 3.** SEM images of sample before modification. (a) SEM of sample before modification, 50x. (b) SEM of sample before modification, 500x.

![Figure 4](image2.png)

**Figure 4.** SEM images of sample after modification. (a) SEM of sample after modification, 50x. (b) SEM of sample after modification, 800x. (c) SEM of sample after modification, 1500x.
a high-temperature and low-oxygen partial pressure. Therefore, the Magnéli phase and Ti$_3$O$_5$ are not present in the slag.

Based on the thermodynamic data obtained from the JANAF database, a plot of the Gibbs free energy of reaction ($\Delta G_r$) versus temperature ($T$) is constructed in Figure 6.

The reaction $3\text{TiO}_2 + \text{Al} = 3/2\text{Ti}_2\text{O}_3 + 1/2\text{Al}_2\text{O}_3$ is the most stable one in both temperature range, which makes Ti$_2$O$_3$ is the most likely to appear in the slag. Furthermore, the reaction $3/2\text{TiO} + \text{Al} = 3/2\text{Ti} + 1/2\text{Al}_2\text{O}_3$ could not proceed spontaneously in the liquid-liquid reactions. Therefore, the reduction reaction is completed in the process of cooling and separation. In the absence of CaO, Ti$_2$O$_3$ and TiO are formed as intermediate products in the reaction process. The density of TiO is close to that of the ferro-titanium alloy (TiO – 5.81 g/cm$^3$, Fe$_2$Ti –

![Figure 5. Relationship of $\log P_{O_2}/P^0$ and T for the phases (calculated from the thermodynamic data of the reaction with 1 mol O$_2$). (a) High-temperature solid–liquid reactions. (b) High-temperature liquid–liquid reactions.](image)

![Figure 6. Relationship between the $\Delta G_r$ and T obtained for the reactions.](image)
6.79 g/cm$^3$, Al$_2$O$_3$ – 3.98 g/cm$^3$, Ti$_2$O$_3$ – 4.57 g/cm$^3$) [18–20]. TiO exists in the alloy structure in the form of inclusions, and Ti$_2$O$_3$ represents a slag.

The calculated phase diagram of the Al$_2$O$_3$–TiO$_2$ system in air is shown in Figure 7(a), while the calculated phase diagram of the Al$_2$O$_3$–Ti$_2$O$_3$ system in the reducing atmosphere ($P_{O_2} = 10^{-16}$ atm) is displayed in Figure 7(b) [21]. If titanium oxide is present in the TiO$_2$ form, corundum and Al$_2$TiO$_4$ species are produced under aluminum-rich conditions. If the titanium oxide phase consists of Ti$_2$O$_3$ species, Al$_2$O$_3$ and Ti$_2$O$_3$ form two independent phases at high temperatures. Only when these phases are separated, the obtained slag can maintain the high melting point and high strength of corundum.

2.3. CaO–TiO$_2$–Al$_2$O$_3$ composite

Both Al$_2$O$_3$ and TiO$_2$ are amphoteric oxides that absorb O$^2^-$ ions to form composite anions in the presence of CaO, which is basic. Hence, after CaO addition, the slags contain TiO$_2$ species. Figure 7(c) shows the liquidus projection of the Al$_2$O$_3$–CaO–TiO$_2$ system [22], which indicates that CaO addition causes a significant decrease in the melting
point of the $\text{Al}_2\text{O}_3$–$\text{TiO}_2$ system and that the obtained $\text{CaO}$–$\text{Al}_2\text{O}_3$ system contains multiple low-melting-point phases. $\text{CaO}$ addition lowers the overall reaction temperature, inducing a partial reduction process. Meanwhile, the viscosity of the liquid decreases, and the interactions between the reactant and reductant become more intense, facilitating further $\text{Ti}_2\text{O}_3$ reduction. However, $\text{TiO}_2$ is not fully consumed by the described reactions and forms a slag compound containing the $\text{Al}_2\text{O}_3$ and $\text{CaO}$ phases.

Figure 8 shows the relationship between the $\Delta G$ and $T$ obtained for the reactions. This means that the order of stable existence of compounds in the system is $\text{CaTiO}_3$, $\text{CA}_6$, $\text{CA}_2$, $\text{CA}$ and $\text{Al}_2\text{TiO}_5$.

2.4. Formation mechanism of $\text{Al}_2\text{O}_3$–$\text{Ti}_2\text{O}_3$ composite

As indicated by the obtained experimental data, the main phase of the slag before adjustment contains $\text{CA}_6$, $\text{CA}_2$, $\text{CaTiO}_3$ and a little corundum, whereas after adjustment it mainly consists of the $\text{Al}_2\text{O}_3$ and $\text{Ti}_2\text{O}_3$ phases.

Only $\text{Ti}^{4+}$ ions are present in material before modification. $\text{CaO}$ and $\text{Al}_2\text{O}_3$ form $\text{CA}_2$, $\text{CA}_6$, and $\text{CaO}$ reacts with $\text{TiO}_2$ to produce $\text{CaTiO}_3$, representing a pure oxide solid solution system [23,24].

$\text{CA}_6$ has many excellent high temperature properties and can be used as a refractory material. $\text{CA}_2$ is easy to hydrate and will be used as a cement material. However, in material before modification, the high temperature performance of $\text{CA}_6$ limits its application as a cement, while $\text{CA}_2$ is easy to hydrate and cannot be used as a high-performance refractory. When $\text{SiO}_2$ is added to the

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Figure 8. Relationship between the $\Delta G$ and $T$ obtained for the reactions.

Figure 9. Reaction model established for material after modification.
system, its melting point can be as low as 1172°C [25]; additionally, the CA2 phase in the material structure is easy to hydrate in air [26]. These characteristics significantly limit the application of the specified material.

Meanwhile, material after modification mainly consists of Ti$^{3+}$ ions, and its smelting is performed in a liquid environment. After thermite, the first crystalized phase from the liquid is the Al$_2$O$_3$ phase (melting point = 2054°C), then the slag begins to solidify, and the separation of alloy and slag ends. TiO$_2$–x compound mixed in Al$_2$O$_3$ exchanges O$^-$ during cooling, and finally Ti$_2$O$_3$ is obtained.

Figure 9 describes the proposed reaction model of material after modification. In this model, TiO$_2$ reacts with Al to form Ti$_2$O$_3$, Ti$_2$O$_3$ reacts with Al to form TiO, TiO reacts with Al to form Ti, and Ti sinks with Fe as Fe$_2$Ti alloy. The Fe$_2$Ti alloy mixed a little TiO$_2$ sinks to the bottom due to its high density, until all of the Al is consumed. After the reaction, the upper layer of the obtained system consists of the molten slag, and its bottom layer consists of the FeTi alloy.

The slag is initially composed of Ti$_2$O$_3$, TiO, and unreacted TiO$_2$. During the cooling process, TiO$_2$ close to TiO will react to form Ti$_2$O$_3$, and TiO$_2$ close to corundum will react to form Al$_2$TiO$_5$. Then the corundum phase is crystallized first followed by Ti$_2$O$_3$ to obtain the two-phase-separated Al$_2$O$_3$–Ti$_2$O$_3$ material.

3. Conclusion

In this study, the ferro-titanium alloy fabrication procedure utilizing the thermite method was considerably improved by CaO free. Based on the thermodynamic analysis, the reaction 3TiO$_2$ + Al = 3/2Ti$_2$O$_3$ + 1/2Al$_2$O$_3$ is the most stable one in high temperature, which makes Ti$_2$O$_3$ is the most likely to appear in the slag. Due to the low solubility of Ti$_2$O$_3$ in Al$_2$O$_3$, the two-phase-separated Al$_2$O$_3$–Ti$_2$O$_3$ material was successfully prepared. The material effectively solves the problem of low melting point caused by CaO and can be used as high-performance refractory.

Disclosure statement

No potential conflict of interest was reported by the authors.

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