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Co-Conversion Mechanisms of Boron and Iron Components of Ludwigite Ore during Reductive Soda-Ash Roasting

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Abstract: Ludwigite ore is a typical intergrown mineral resource found in China. Reductive soda-ash roasting followed by water leaching is an innovative process for the high-efficiency separation and recovery of boron and iron. In this study, the co-conversion mechanism of boron activation and iron reduction during soda-ash reductive roasting for boron-bearing iron concentrate was clarified. When the boron-bearing iron concentrate was reduced in the presence of Na₂CO₃, szaibelyite (Mg₂(OH)(B₂O₄) (OH)) was activated to sodium metaborate (NaBO₂) and, meanwhile, magnetite (Fe₃O₄) was reduced to metallic iron (MFe). Boron activation promoted iron-oxide reduction effectively, while the latter could only slightly influence the former. The promotion occurred through (1) a facilitated generation of sodium magnesium silicate (Na₂MgSiO₄) and a hindering of the formation of olivine (Mg_xFe_{2-x}(SiO₄)). (2) The newly generated NaBO₂ promoted iron-oxide reduction. (3) The low melting point of the NaBO₂ (966 °C) favored particle migration, which accelerated metallic iron particle aggregation.

Keywords: ludwigite ore; soda-ash; reduction; activation; co-conversion

1. Introduction

Boron and its compounds are used in the chemical, medicinal, and nuclear industries [1–3]. Due to their extensive application in areas such as electronic products, advanced materials, and new energy vehicles, boron resources are designated as indispensable mineral resources for emerging strategic industries [4–6]. Chinese boron reserves rank fifth globally at 24 million tons (B₂O₃) [7]. Despite the high reserves, boron-bearing ore exploitation is limited because of its complex mineralogy [8], which leads to a high reliance on imports. The gradual depletion of szaibelyite ore has led to the development and use of ludwigite ore with abundant reserves to ensure the sustainable development of China's boron industry [9].

The current plan for ludwigite ore processing is to separate boron and iron magnetically with gravity processing to yield a boron-bearing iron concentrate, boron concentrate, and uranium concentrate [10]. The boron-bearing iron concentrate is smelted in a blast furnace, the boron concentrate is used to produce borax/boric acid, and uranium is extracted hydro metallurgically from the uranium concentrate [11,12]. However, because of the complex mineralogy in which boron, iron, and magnesium are intergrown, boron and iron are difficult to separate completely by using physical dressing techniques, which results in the dispersed distribution of boron compounds.



Boron-bearing iron concentrate is a magnetic product that is produced from the magnetic separation of ludwigite ore with a boron distribution of 30%. Pyrometallurgical processing [13–15] is usually used for boron and iron separation in boron-bearing iron concentrate because of the high iron content. Despite the good boron–iron separation performance, the high operating temperature (~1500 °C) in the pyrometallurgical process results in B₂O₂ volatilization and a low boron-bearing slag activation [16]. Because of the low alkaline hydrolysis of boron, in the carbon-dioxide–soda process, 4 to 5 tons of boron mud will be generated per ton of borax produced [17,18]. Thus, boron-bearing iron concentrate can only be used as steel-making material, which leads to boron resource wastage. It is clear that a low resource utilization, high solid-waste discharge, and serious environmental pollution accompany current ludwigite ore exploitation processes. Hence, breakthrough techniques for cleaner and highly efficient ludwigite ore utilization are required urgently.

These challenges led our research group to demonstrate that iron-oxide reduction and boron activation could be achieved simultaneously through soda-ash introduction during direct reduction, and, thus, a new high-efficiency boron–iron separation and recovery process based on sodium reduction and water leaching was developed [19–21]. Compared with the existing process, the new process separates boron and iron via magnetic separation and extracts boron and sodium from grinding and water-leaching solutions. Furthermore, 95.70% iron was recovered as powdery metallic iron in the magnetic concentrate at a reduction temperature of 1050 °C and time of 60 min with 20 wt.% Na₂CO₃. Subsequently, 96.97% Na₂O and 96.86% B₂O₃ were extracted into the leach liquor at a leaching temperature of 200 °C and a liquid-to-solid mass ratio of 8:1. This approach avoided boron mud production and excessive alkali pollution.

The co-conversion mechanism of iron reduction and boron activation during soda-ash roasting of boron-bearing iron concentrate is key to the development of a new process. In this study, the effect of Na₂CO₃ dosage and roasting conditions on the boron activation and the reduction of iron oxides was investigated by using a boron-bearing iron concentrate as a raw material combined with inductively coupled plasma-optical emission spectroscopy (ICP-OES), thermogravimetry-mass spectroscopy (TG-MS), X-ray diffractometry (XRD), and electron probe micro-analysis (EPMA). To provide sufficient theoretical proof for high-efficiency boron–iron separation and extraction, the principles of thermal behavior as well as phase and microstructural transformations during soda-ash roasting of the boron-bearing iron concentrate were determined, and the synergistic relationship between boron activation, iron-oxide reduction, and metallic iron particle growth was established.

2. Materials and Methods

2.1. Materials

The boron-bearing iron concentrate contained 52.1% Fe_{total}, 5.3% B₂O₃, 12.6% MgO, and 5.4% SiO₂, as listed in Table 1, and mainly magnetite, szaibelyite, lizardite, and magnesite, as shown in Figure 1a. Figure 1b indicates that 91.1% of the iron was distributed in magnetite, whereas 95.9% of the boron was distributed in szaibelyite.

Chemical reagents, including Na₂CO₃ (99.95%), NaBO₂·4H₂O (99.95%), and high-purity gases (CO, 99.5 vol.%, N₂, 99.999 vol.%) were used.

Table 1. Main chemical compositions of boron-bearing iron concentrate (mass fraction, %).

TFe	FeO	B_2O_3	SiO ₂	MgO	CaO	Na ₂ O	Al ₂ O ₃	S	LOI *
52.1	24.7	5.3	5.4	12.6	0.6	0.2	0.4	0.2	2.5
* LOI: loss on ignition.									



Figure 1. (a) X-Ray Diffraction pattern of boron-bearing iron concentrate. (b) Distributions of Fe, B, Mg, and Si in the main phases.

2.2. Methods

2.2.1. Soda-Ash Roasting

The ground boron-bearing iron concentrate and Na₂CO₃ were mixed thoroughly for briquetting. Green briquettes were dried at 110 °C for 2 h in a drying oven. Soda-ash roasting tests were carried out in a vertical electric resistance furnace, as shown in Figure 2. CO (99.5%) and N₂ (99.999%) were used as the reducing and protective gas, respectively. The gas flow rates were fixed at 200 L/h. N₂ was introduced into a stainless-steel tank (inner diameter of 20 mm) in the furnace and preheated to a set temperature. The tank was loaded with ~10 g of dry briquettes, and the atmosphere was converted to CO. After roasting, the gas was changed from CO to N₂, and the tank was removed from the furnace to allow for cooling to room temperature. A portion of the roasted briquettes was ground to pass a 200-mesh standard sieve to determine the chemical composition and for water leaching, and some briquettes were mounted and polished for microstructural analysis.



Figure 2. Schematic diagram of experimental device for soda-ash roasting [21].

2.2.2. Water Leaching

Boron activation was determined from water leaching in a glycerin-bath autoclave, as shown in Figure 3. The roasted sample (particle size $< 74 \mu m$) and deionized water in a certain mass ratio were added into the pots and rotated at 20 rpm for leaching. When the predetermined leaching time was

reached, the pots were removed for cooling. The pulp was filtered in a vacuum filter, and the leach liquor and filtered residue chemical content were determined by inductively coupled plasma-optical emission spectroscopy.



Figure 3. Schematic diagram of the experimental device for water leaching [21].

2.2.3. Characterization

The main chemical compositions of boron-bearing iron concentrate were determined by X-ray fluorescence (XRF, Axios, PANalytical B.V., Almelo, Netherlands), while the content of B_2O_3 was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, 8300, PerkinElmer, Waltham, MA, USA) and the content of metallic iron in roasted samples was determined by chemical titration. The phase compositions of boron-bearing iron concentrate and roasted samples were analyzed by X-ray diffraction (XRD, D8 Advance, BRUKE, Karlsruhe, Germany) with a scan speed of 5°/min. Microstructures of roasted samples were performed by an optical microscope (Leica, DM 4500P, Weztlar, Germany) and the elemental distributions of B, O, Si, Mg, Fe, and Na in reduced samples were determined by an electro-probe microanalyzer (EPMA, JXA-8230, JEOL, Tokyo, Japan). Simultaneous thermogravimetric-differential scanning calorimetry analyses (TG-DSC, STA449 F5, NETZSCH, Selb, Germany) were performed in an α -alumina sample holder at a heating rate of 10 °C/min under an argon atmosphere to evaluate the thermal behavior of the mixtures. Meanwhile, the examinations of the mixtures were supplemented with gas analysis by using a mass spectrometry (MS, QMS 430D, NETZSCH, Selb, Germany). The contact angles were determined by a high-temperature contact angle measurement instrument (OCA 25LHT, Dataphysics, Stuttgart, Germany) with a maximum operating temperature of 1700 °C and a heating rate of 5 °C/min.

3. Results and Discussion

3.1. Determination of Boron Activation

The activation of the boron components refers to the phase transformation of magnesium borate to sodium borate during soda-ash roasting. The boron activation was defined as the percentage of boron in sodium borate to the total boron content in the roasting products, as calculated from Equation (1).

$$\alpha(w) = \frac{V_1 \times c_1}{m_0 \times c_0} \times 100\% \tag{1}$$

where $\alpha(w)$ is the boron activation, m_0 is the mass of roasting sample, c_0 is the boron grade of the roasting sample, V_1 is the leach liquor volume, and c_1 is the boron concentration in the leaching solution.

The chemical phase distribution of boron in the roasting sample is difficult to confirm by chemical titration. However, a significant difference exists between the water solubility of sodium borate and magnesium borate, as shown in Figure 4. The water solubility of NaBO₂ was 4.3 mol/L at room temperature, while the water leaching rate of B of $Mg_2B_2O_5$ and $Mg_3B_2O_6$ was merely 2.9% and 1.2%,

respectively. Therefore, water leaching was used to determine the boron activation. During water leaching, insoluble boron in magnesium borate and boron that had dissolved completely in sodium borate were used as the criteria for boron activation.



Figure 4. Solubility in water of (**a**) NaBO₂, (**b**) Mg₂B₂O₅ (purity 94.1%), and (**c**) Mg₃B₂O₆ (purity 93.0%) at different leaching temperatures.

Based on the solubility of sodium borate and magnesium borate at different water leaching temperatures, a water leaching temperature of 90 °C, leaching time of 6 h, and liquid-solid ratio of 8:1 was selected as the conditions for boron activation.

3.2. Effect of Roasting Conditions on Boron Activation

The effect of Na_2CO_3 dosage on the boron activation was investigated at a reduction temperature of 1000 °C for a reduction time of 60 min. The results are shown in Figure 5a. As the Na_2CO_3 dosage increased from 5 wt.% to 20 wt.%, the boron activation increased from 29.0% to 93.0%, respectively.



Figure 5. Effect of roasting conditions on boron activation (**a**) Na₂CO₃ dosage; (**b**) Reduction temperature; (**c**) Reduction time.

The chemical and phase composition of the boron-bearing iron concentrate indicated that Na_2CO_3 reacted mainly with szaibelyite and lizardite in a reduction roasting process. The theoretical dosages of Na_2CO_3 that were required for conversion of $Mg_2(OH)(B_2O_4)$ (OH) to $NaBO_2$ and $Mg_3Si_2O_5(OH)_4$ to Na_2MgSiO_4 were 8.1 wt.% and 9.5 wt.%, respectively, as calculated from Equations (2) and (3). Thus, when the Na_2CO_3 dosage was 5 wt.%, the boron activation was only 29.0%.

$$Mg_{2}(OH)(B_{2}O_{4})(OH)(s) + Na_{2}CO_{3}(s) = 2NaBO_{2}(s) + CO_{2}(g) + H_{2}O(g) + 2MgO(s)$$
(2)

$$Mg_{3}Si_{2}O_{5}(OH)_{4}(s) + 2Na_{2}CO_{3}(s) = 2Na_{2}MgSiO_{4}(s) + 2CO_{2}(g) + 2H_{2}O(g) + MgO(s)$$
(3)

When the Na₂CO₃ dosage was increased to 10 wt.%, the boron activation was 53.7%. Although the theoretical stoichiometric dosage of Na₂CO₃ for the activation of boron components had been exceeded, the boron component activation was low. Figure 6 shows the main conversion reactions during reductive soda-ash roasting. Standard Gibbs free energies of the related reactions were calculated using FactSage 7.2 in the temperature range 400–1400 °C. Our previous studies [22] indicated a szaibelyite dehydroxylation product of Mg₂B₂O₅ could be converted easily into Mg₃B₂O₆ in the presence of Na₂CO₃, as shown in Figure 6 (Equation (4)). Since the reaction tendency of Mg₂SiO₄ with Na₂CO₃

exceeded that of $Mg_3B_2O_6$, as shown in Figure 6 (Equations (5)–(7)), a lizardite dehydroxylation product of Mg_2SiO_4 would react preferentially with Na_2CO_3 , which hindered further conversion of $Mg_3B_2O_6$ to $NaBO_2$ when the Na_2CO_3 dosage was insufficient. When the Na_2CO_3 dosage was increased to 20 wt.%, the boron activation reached 93.0%.

$$3Mg_2B_2O_5(s) + Na_2CO_3(s) = 2NaBO_2(s) + 2Mg_3B_2O_6(s) + CO_2(g)$$
 (4)

$$Mg_2SiO_4(s) + Na_2CO_3(s) = Na_2MgSiO_4(s) + MgO(s) + CO_2(g)$$
 (5)

$$Mg_{2}B_{2}O_{5}(s) + Na_{2}CO_{3}(s) = 2NaBO_{2}(s) + 2MgO(s) + CO_{2}(g)$$
(6)

$$Mg_{3}B_{2}O_{6}(s) + Na_{2}CO_{3}(s) = 2NaBO_{2}(s) + 3MgO(s) + CO_{2}(g)$$
(7)



Figure 6. Plots of Gibbs free energy against the temperature for different reactions.

The effect of the reduction temperature on the boron activation is shown in Figure 5b for a fixed Na_2CO_3 dosage of 20 wt.% and a reduction time of 60 min. The boron activation increased from 48.9% to 90.1% as the reduction temperature increased from 600 °C to 800 °C. When the temperature exceeded 800 °C, the activation changed only slightly.

For a constant reduction temperature of 1000 °C and an Na₂CO₃ dosage of 20 wt.%, the influence of reduction time on the boron activation is shown in Figure 5c. The boron activation was affected less by the reduction time. The boron activation reached 90.2% when the reduction time was 5 min. The boron activation varied only slightly with the roasting atmosphere. When the boron-bearing iron concentrate was roasted at 1000 °C for 60 min with 20 wt.% Na₂CO₃, the boron activation was 94.5%, 93.3%, and 93.0% in air, pure nitrogen, and pure carbon oxide, respectively, which indicates that iron-oxide reduction had little effect on the boron component activation. This behavior occurred because the boron phase in the boron-bearing iron concentrate existed mainly in szaibelyite and only 4.1% of the boron occurred in ludwigite, as shown in Figure 1b.

In conclusion, the boron activation was influenced significantly by the Na_2CO_3 dosage and reduction temperature. For the boron activation to exceed 90%, the Na_2CO_3 dosage should exceed 20 wt.% and the reduction temperature should exceed 800 °C. Furthermore, magnesium borate could be activated rapidly to sodium borate for a reduction temperature up to 1000 °C.

3.3. Effect of Roasting Conditions on Iron-Oxide Reduction

3.3.1. Iron-Oxide Metallization

The variation of iron-oxide metallization was investigated in the boron component activation. The effect of Na_2CO_3 dosage on the iron metallization was explored for a reduction temperature of 1000 °C and a reduction time of 60 min. The results are shown in Figure 7a. Since the iron phase in the boron-bearing iron concentrate existed mainly as easily reduced magnetite, the iron

metallization was 84.4% in the absence of Na₂CO₃. With Na₂CO₃ addition, the iron metallization increased. According to the above results, 9.5 wt.% Na₂CO₃ was required for the transformation from Mg₃Si₂O₅(OH)₄ to Na₂MgSiO₄, whereas Na₂MgSiO₄ formation was beneficial for the iron-oxide reduction by impeding the reaction between FeO and Mg₂SiO₄. Thus, iron metallization reached 91.0% when the Na₂CO₃ dosage was increased to 10 wt.%. No evident changes resulted with a further increase in Na₂CO₃ dosage.



Figure 7. Effect of roasting conditions on iron metallization in reduction products (**a**) Na₂CO₃ dosage; (**b**) sodium borate dosage; (**c**) Reduction temperature; (**d**) Reduction time.

To investigate the influence of boron component activation on the reduction of iron oxides, the effect of NaBO₂·4H₂O dosage on iron metallization at a constant reduction temperature of 1000 °C and a reduction time of 60 min was studied, and the results are shown in Figure 7b. NaBO₂·4H₂O addition could promote iron-oxide reduction during the roasting of boron-bearing iron concentrate. When the NaBO₂·4H₂O dosage was 4 wt.%, the iron metallization exceeded 90%. Studies have shown that borax with sodium ion and borate anion groups could accelerate the reduction of iron oxide and reduce the reaction activation energy during reduction [23].

As shown in Figure 7c,d, the iron metallization increased visibly with an increase in reduction temperature and an extension of reduction time. With a fixed Na₂CO₃ dosage of 20 wt.% and a reduction time of 60 min, the iron metallization was only 1.5% at a reduction temperature of 600 °C, which indicates that the magnetite in the boron-bearing iron concentrate had not been reduced to metallic iron. At an increased reduction temperature of 800 °C, the iron metallization was 61.0%, which showed a significant improvement when compared with that at 700 °C. When the reduction temperature of 1000 °C, the iron metallization reached 91.7%. At a constant reduction temperature of 1000 °C and an Na₂CO₃ dosage of 20 wt.%, the iron metallization was only 20.8% when the reduction time was 5 min. Compared with the conversion of boron components, the boron activation reached 90.2% under the same roasting conditions, which shows that the reduction of iron oxide had little effect on the boron component activation. Since the reduction time was extended to 60 min, the iron metallization reached 91.7%.

3.3.2. Metallic Iron Particle Growth

The activation of boron components and the metallic reduction of iron oxides was the foundation for the simultaneous separation of boron and iron in soda-ash roasting, whereas metallic iron particle growth was key to the efficient separation of boron and iron in subsequent magnetic separation because the average size of the metallic iron particles influenced the iron grade and iron concentrate recovery directly. At a fixed reduction temperature of 1000 $^{\circ}$ C and a reduction time of 60 min, the effects of Na₂CO₃ dosage on the growth of metallic iron particles are shown in Figure 8.



Figure 8. Microstructures of polished cross-section and volume frequency distribution of metallic iron particles of reduced boron-bearing iron concentrate pellets obtained at 1000 °C for 60 min for different Na₂CO₃ dosages (**a**) 0 wt.% Na₂CO₃ dosages; (**b**) 5 wt.% Na₂CO₃ dosages; (**c**) 10 wt.% Na₂CO₃ dosages; (**d**) 15 wt.% Na₂CO₃ dosages; (**e**) 20 wt.% Na₂CO₃ dosages; (**f**) volume frequency.

Figure 8 shows that the increase of Na_2CO_3 favored metallic iron particle growth. When the boron-bearing iron concentrate was reduced without Na_2CO_3 , the metallic iron particles were fine, and the distribution interval was 0–133 µm with the proportion of largest particle size being only 2.6%. When the Na_2CO_3 dosage was increased to 10 wt.%, the boron activation was 53.6% and the metallic iron particles began to agglomerate but remained intergrown with other gangue minerals. The microstructure changed significantly as the Na_2CO_3 dosage increased to 15 wt.%. The size of the metallic iron particles increased and aggregated into rings with a corresponding boron activation of 81.1%. The continuous increase of Na_2CO_3 dosage highlighted the ring-shaped metallic iron particles in the microstructure image. The distribution interval of metallic iron particles was extended to 0–204 µm and the volume frequency of 204 µm was 8.6% in the presence of 20 wt.% Na_2CO_3 , which created an excellent condition for subsequent grinding and magnetic separation.

3.4. Mechanisms in Co-Conversion of Iron and Boron Components

3.4.1. TG-MS/DSC Analysis

To identify the interaction between the activation of boron components and the reduction of iron oxides in roasting, boron-bearing iron concentrate, and graphite were mixed in a carbon: iron molar ratio of 2:3 in the absence/presence of Na₂CO₃, and TG-MS analysis was performed on the mixtures in argon with the results shown in Figure 9.

The mixture without Na₂CO₃ addition (Figure 9a) had two clear mass loss peaks in the DTG curve during roasting, and the total mass loss was 22.6%. A mass loss occurred around 621 °C from magnesite decomposition and lizardite and szaibelyite dehydroxylation, whereas the mass loss at 1073 °C resulted because of the reduction of iron oxides. The actual mixture mass loss was 75.5% of the theoretical value, and the temperature range for iron-oxide reduction was 950–1150 °C.

As shown in Figure 9b, four mass loss peaks and three CO_2 -evolution peaks were observed when the mixture was heated from 25 °C to 1400 °C with the addition of 20 wt.% Na₂CO₃. The total mass loss was 29.7%, which was 93.7% of the theoretical value and 18.2% higher than that without Na₂CO₃. A mass loss peak of 1.6% at 108 °C resulted because of crystallization water dehydration. The second mass loss peak of 11.4% was distributed between 470 °C and 770 °C with the release of CO_2 . To ascertain which reactions corresponded to the mass loss, TG-DSC of a mixture of lizardite (purity 96.2%), szaibelyite (purity 94.3%), and sodium carbonate with a molar ratio of 1:1:3 was carried out with the result shown in Figure 10.



Figure 9. TG-MS results of mixture of boron-bearing iron concentrate and graphite with carbon: iron molar ratio of 2:3 in argon (**a**) in the absence of Na₂CO₃ and (**b**) in the presence of 20 wt.% Na₂CO₃.



Figure 10. TG-DSC result of lizardite, szaibelyite, and sodium carbonate mixture with molar ratio of 1:1:3 in argon.

In Figure 10, three clear mass loss peaks occur in the DTG curve during roasting with three corresponding endothermic peaks in the DSC curve. The mass loss peak of 4.7% at 94 °C resulted mainly because of crystallization water dehydration. According to the mixture molar ratio, the theoretical mass loss from lizardite and szaibelyite dehydroxylation was 2.4% and 4.7%, respectively. The reactions between dehydroxylation products and Na₂CO₃ was the other reason for the mass loss of 12.5% at 584 °C. The mass loss of 10.0% occurred at 714 °C because of the continuing sodium reactions. Hence, the temperature interval for the reactions between lizardite/szaibelyite and Na₂CO₃ was 450–750 °C, which explains the second mass loss peak in Figure 9b. Our previous research proved that the reaction between the dehydroxylation products of lizardite and Na₂CO₃ were dependent on the melting of Na₂CO₃ (851 °C) [22]. Nevertheless, the mixture mass loss ended at ~750 °C in the presence of szaibelyite, which indicates that szaibelyite activation facilitated the reaction between lizardite and Na₂CO₃, which favored iron-oxide reduction.

As the temperature increased, a mass loss with CO_2 release appeared at 843 °C owing to the excess Na_2CO_3 decomposition with a thermal decomposition temperature of 851 °C in Figure 9b. The mass loss started at 880 °C and ended at 1015 °C with massive CO_2 and CO gas emissions because of the reduction of iron oxides, which showed that Na_2CO_3 addition could reduce the iron-oxide reduction temperature. Therefore, boron activation (450–750 °C) took precedence over iron-oxide reduction (880–1015 °C) of born-bearing iron concentrate during reductive soda-ash roasting, which could provide a favorable condition for iron-oxide reduction.

3.4.2. Phase Transformation

The Na_2CO_3 dosage and roasting temperature had a significant impact on the phase transformation of reduced boron-bearing iron concentrate, as shown in Figure 11.



Figure 11. (a) Effect of Na₂CO₃ dosage on phase transformation of reduced boron-bearing iron concentrate at 1000 °C for 60 min. (b) Effect of roasting temperature on phase transformation of boron-bearing iron concentrate reduced for 60 min with 20 wt.% Na₂CO₃. Ff-Forsterite ferroan (Mg_xFe_{2-x}(SiO₄)), Mfo-Magnesium ferrous oxide ((MgO)_x(FeO)_{1-x}), M-Magnetite (Fe₃O₄), Fo-Forsterite (Mg₂SiO₄), F-Ferrous oxide (FeO), I-Iron (Fe), Ic-cementite (Fe₃C), Ko-Kotoite (Mg₃B₂O₆), Dm-Magnesium disodium silicate (Na₂MgSiO₄), P-Magnesia (MgO), and Sb-Sodium metaborate (NaBO₂).

Figure 11a shows that reduction transformed the original magnetite (Fe₃O₄) phase in the boron-bearing iron concentrate to olivine (Mg_xFe_{2-x}(SiO₄)) and metallic iron (Fe) in the presence of 0 wt.% or 5 wt.% Na₂CO₃. The formation of olivine (Mg_xFe_{2-x}(SiO₄)) was the main reason for the low iron metallization. An increase of Na₂CO₃ dosage to 10 wt.% led to the disappearance of forsterite ferroan (Mg_xFe_{2-x}(SiO₄)) with the generation of magnesium ferrous oxide ((MgO)_x(FeO)_{1-x}) and magnesium disodium silicate (Na₂MgSiO₄), which was favorable for iron-oxide reduction. Figure 11b shows XRD patterns of boron-bearing iron concentrate that was reduced at various temperatures in the presence of 20 wt.% Na₂CO₃. At low temperatures (\leq 700 °C), cementite (Fe₃C) was the main iron component phase, which impeded the iron-oxide reduction. When the reduction temperature exceeded 800 °C, the cementite (Fe₃C) phase disappeared with more and stronger metallic iron diffraction peaks. Kotoite (Mg₃B₂O₆) was the main boron component phase when the Na₂CO₃ dosage was less than 10 wt.% and the reduction temperature was lower than 700 °C during roasting. With an increase of Na₂CO₃ dosage and roasting temperature, kotoite was transformed into sodium metaborate (NaBO₂). Thus, a key point of boron component activation was the phase transformation from Mg₃B₂O₆ to NaBO₂ of boron-bearing iron concentrate during direct reduction.

Therefore, the original phases of magnetite (Fe₃O₄) and szaibelyite (Mg₂(OH)(B₂O₄) (OH)) in the boron-bearing iron concentrate could transform simultaneously into metallic iron and sodium borate by controlling the roasting temperature and Na₂CO₃ dosage during direct reduction. The phase compositions of boron-bearing iron concentrate that was reduced at 1000 °C for 60 min in the presence of 20 wt.% Na₂CO₃ were metallic iron (MFe), sodium borate (NaBO₂), magnesium disodium silicate (Na₂MgSiO₄), and magnesia (MgO).

The wetting ability can be described as the ability for phases to bond or adhere at the point of interfacial contact, which is quantified through the contact angle (θ) that forms at the solid/liquid interface. A contact angle that varies between 0° and 90° implies a strong wettability, whereas a contact angle that exceeds 90° implies a weak wettability [24]. To investigate the effect of sodium products on the growth of metallic iron particles, contact angle measurements with a shape fit-differential method [25,26] of NaBO₂-Fe and Na₂MgSiO₄-Fe were conducted. The results are shown in Figure 12.



Figure 12. Contact angles at different roasting temperatures. (a) NaBO₂-Fe and (b) Na₂MgSiO₄-Fe.

Figure 12 shows that the contact angle (θ) between NaBO₂ and Fe decreased with an increase in roasting temperature, especially when the roasting temperature exceeded 900 °C. The contact angle between NaBO₂ and Fe decreased to 47.3° as the temperature increased to the melting point of NaBO₂ (966 °C). The contact angle decreased sharply to 24.3°, when the roasting temperature was increased to 1000 °C.

Figure 12b shows that the contact angle between Na_2MgSiO_4 and Fe also decreased with an increase in roasting temperature, and this decrease was rapid when the temperature exceeded 1300 °C. The contact angle between Na_2MgSiO_4 and Fe decreased to 68.1° as the temperature increased to 1340 °C. As the temperature increased to 1450 °C, the contact angle decreased rapidly to 30.8°.

In comparison, the wettability of NaBO₂ to Fe was much better than that of Na₂MgSiO₄. Therefore, the activation of boron components was the fundamental reason for the acceleration of metallic iron particle growth during direct reduction of boron-bearing iron concentrate in the presence of Na₂CO₃, which implied that the metallic iron particles were fine when the boron activation was low, as shown in Figure 8.

3.4.3. Microstructure

To verify the above analysis, the elemental distributions of B, O, Si, Mg, Fe, and Na in the boron-bearing iron concentrate pellets that were reduced at 1000 °C for 60 min with/without Na₂CO₃ were determined by electron probe micro-analysis, as shown in Figure 13. The distribution of B and Si was consistent with that of Mg in the absence of Na₂CO₃, and agreed with the phase compositions in Figure 13a. The intergrown distribution of metallic iron particles with the high-melting-point minerals (Mg₃B₂O₆: 1350 °C, Mg₂SiO₄: 1890 °C) was the dominant reason for the fine metallic iron particles.

The elemental distribution changed significantly in the presence of 20 wt.% Na₂CO₃, as shown in Figure 13b. The distribution of B and Si agreed with that of Na with the formation of NaBO₂ and Na₂MgSiO₄. The low-melting-point sodium metaborate (NaBO₂: 966 °C) was distributed along the ring-shaped metallic iron particles and facilitated particle migration and diffusion.



Figure 13. Elemental mapping of reduced boron-bearing iron concentrate pellets (**a**) without and (**b**) with 20 wt.% Na₂CO₃ by EPMA analysis.

4. Conclusions

Boron activation took precedence over iron-oxide reduction of ludwigite ore during reductive soda-ash roasting. It was affected by the Na_2CO_3 dosage, while being less influenced by the roasting time and atmosphere. When Na_2CO_3 dosage was 20 wt.%, the boron activation was 90.2% at a reduction temperature of 1000 °C and for a reduction time of 5 min. The high-efficiency activation of magnesium borate favored the boron extraction in the subsequent grinding and water leaching, avoiding the boron mud production. Iron-oxide reduction was promoted by boron activation through a facilitated reaction between lizardite and soda-ash and a hindering of the formation of olivine. A szaibelyite activation product of NaBO₂ could accelerate iron-oxide reduction and metallic iron particle growth. When the sodium-metaborate dosage increased from 0% to 4%, the iron metallization increased from 84.4% to 90.1%. The contact angle between NaBO₂ (melting point of 966 °C) and Fe was 24.3° at the roasting temperature of 1000 °C, implying a strong wettability to the metallic iron particle. When the boron activation was 93.0%, the iron metallization was 91.7% and the distribution interval of metallic iron particles widened to $0-204 \,\mu\text{m}$ with a volume frequency at 204 μm of 8.6%, facilitating iron separation and recovery. On the basis of reductive soda-ash roasting, the main valuable elements of boron and iron in ludwigite ore can be separated and recovered effectively by magnetic separation and water leaching.

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