Phase Development in the Sintering of a Hematite–Ilmenite Ore Blend

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Received: 8 August 2020; Accepted: 8 September 2020; Published: 11 September 2020

Abstract: The use of low-grade iron ores has attracted a lot of interest where fines from these ores are sintered to improve their strength. Ti-containing ores are one of the abundantly available iron ores of low-grade. The sintering of the hematite–ilmenite ore blends has several challenges, which include the formation of perovskite. The sintering behavior of a hematite–ilmenite ore sinter blend was investigated in 75 vol% N₂, 24 vol% CO₂, and 1 vol% CO in the temperature range of 1373 to 1523 K. Phase development and distribution of metallic elements were investigated by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and electron probe microanalysis (EPMA). The addition of ilmenite ore to hematite ore increased the temperature of melt formation. More titanium (Ti) was distributed in the glass phase with increasing temperature. Morphological change showed that the amount of sinter-bonding phase generated was low, below 1473 K. Weak sinter bonding strength might be caused by the presence of Ti in the glass phase at high temperature. This might affect the fracture toughness of the glass phase.

Keywords: sintering; phase development; element distribution; melt formation; perovskite

1. Introduction

The growth in the steel industry has increased the demand of high-grade iron ores, which have been depleted, and hence requires investigation of how to utilize low-grade ores such as titanium-containing ores. In the sintering of iron ore, titanium can be introduced into the sinter mix when adding ilmenite, FeO-TiO₂(s), or titanomagnetite, Fe₃₋xTiₓO₄(s). Ti-containing ores, as a cheap source of iron, can introduce small amounts of TiO₂(s) into the furnace that could lead to the protection of the hearth lining by forming complex carbo-nitrides. In addition, small amounts of Ti can also enter into the molten iron, leading to Ti-containing steels with improved mechanical properties [1]. Moreover, the blast furnace slag from Ti-bearing sinter can be used as a secondary titanium resource. Some researchers [2] have used NaOH to decompose the high Ti slags, where titanium is converted to sodium titanate, then titanium dioxide is obtained after acidolysis, heating hydrolysis, and calcination. This will enable the maximum utilization of the Ti-containing resources. However, during sintering, Ti has been reported to negatively affect the sinter properties due to the formation of perovskite [3–5].

Addition of iron sand, known as titanomagnetite, ores to iron ore sinter blends was investigated, and showed that most of the Ti was distributed in the glass phase after sintering [3]. This lowered the mechanical strength of the glass phase and enhanced the crack propagation causing the reduction in the degradation index (RDI) deterioration.

The addition of TiO₂(s) was reported [1] to affect the development of bonding phase due to the presence of CaO-TiO₂(s). The sinter phases observed after firing the sinter mix containing about 2 wt% TiO₂ at 1553 K were composed of silico-ferrite of calcium and aluminum (SFCA), Fe₂O₃(s), Fe₃O₄(s), 2CaO-SiO₂(s), and CaO-TiO₂(s) [1]. The sintering behavior and consolidation mechanism...
of high-chromium vanadium and titanium magnetite fines showed that the amount of liquid phase generated in these sinters was low compared with that formed in ordinary iron ore sinter [5]. Furthermore, some perovskite replaced the calcium ferrite, which resulted in the decreased strength of the bonding phase. The dissected vanadium-bearing titanomagnetite sinter bed showed that most of the perovskite was likely to be formed in the high temperature region [4]. The suggested formation of perovskite was as follows. The TiO$_2$ in titanomagnetite reacted with calcium oxide in melt at high temperature. Hematite, perovskite, and dicalcium silicate precipitated out of melt. Hematite exists between the magnetite and silicates. Volume expansion from hematite reduction was responsible for RDI deterioration [4]. Some researchers [4–6] have suggested that perovskite formation occurs rapidly at temperatures higher than the melting point of SFCA, hence low temperature-sintering methods have been proposed.

In the investigation of the effects of sintering materials and gas conditions on the formation of SFCA during iron ore sintering, iron sand remained unreacted at 1523 K, and even at temperatures of around 1598 K, some unreacted iron sand existed in the sample [7]. However, thermodynamics showed that in the presence of CaO(s), TiO$_2$(s) should readily react to form perovskite [8].

Since TiO$_2$(s) is incorporated into the sinter mix in the form of FeO-TiO$_2$(s) or Fe$_{3−x}$Ti$_x$O$_4$(s), the detachment of TiO$_2$(s) from FeO-TiO$_2$(s) or Fe$_{3−x}$Ti$_x$O$_4$(s) and the diffusion of metallic ions such as Ca$^{2+}$ and Mg$^{2+}$ into the Ti-rich iron phase might have an influence on the formation of CaO-TiO$_2$(s). Ti-containing ores are characterized by a variety of chemical and mineralogical composition [9]. The form in which TiO$_2$(s) exist and the interactions of the Ti-parent phase with other metallic elements in the sinter might affect the release mechanism of TiO$_2$(s) for the formation of perovskite. The current study aims to investigate the change in phase and elemental distribution in a sinter blend of hematite-ilmenite ore in the temperature range of 1373 to 1523 K in order to determine where Ti might be located in the sinter with increasing temperature. The ilmenite ore was used in this investigation because it contains more TiO$_2$ than the titanomagnetite, and adjustment of the TiO$_2$ in the hematite ore to levels where identifiable perovskite could be formed was done with the minimum addition of the ilmenite ore. This ensured the minimum addition of the other gangue components in the hematite ore as compared to using titanomagnetite. An example of titanomagnetite that has been widely researched is iron sand with a TiO$_2$ content of around 8 wt% [10]. The ilmenite ore used in this experiment had a TiO$_2$ content of around 19 wt%. This might provide a better understanding of the phases formed and the possible interactions of the Ti-enriched Fe phase with other metallic components as the temperature increased. The effect of adding ilmenite ore to the hematite ore on the temperature of melt formation was also investigated. Since the formation of perovskite in the sintering of Ti-containing ores has been reported to negatively affect the sinter strength [1,3], it is wise to determine the temperature range at which most of the perovskite might be formed. The research outcome will be utilized to assess whether low temperature sintering favors the formation of a lower amount of perovskite. This information might be used in developing a low temperature iron ore sintering method.

2. Materials and Methods

2.1. Material Preparation

The chemical composition of the material used in this experiment is shown in Table 1. The particle sizes of the hematite and ilmenite ores were less than 250 µm. The use of this small particle size enabled the uniform mixing of the ores; however, in the actual sintering process, ores with large particle sizes are used. The TiO$_2$ content in the hematite and ilmenite ores were 0.22 and 18.9 wt%, respectively. The phases in the samples were identified by x-ray diffraction (XRD, Bruker AXS) using a Cu tube at a scan angle of 20° to 80°, a rate of 2°/min, sampling 0.02° at a voltage of 40 kV and current of 40 mA. The XRD analysis showed that the major phases in the hematite ore were Fe$_2$O$_3$(s), 3CaO-3Al$_2$O$_3$-SiO$_2$(s), and SiO$_2$(s) (Figure 1). The ilmenite ore consisted of Fe$_5$O$_4$(s), SiO$_2$(s), ilmenite (Fe$_{1.04}$Ti$_{0.94}$O$_3$(s)), and calcium iron vanadium oxide (3CaO-Fe$_2$O$_3$-FeO-V$_{1.5}$Fe$_{0.5}$O$_5$(s)) as the primary phases.
Temperature was non-isothermally raised at a rate of 20 K/min from 298 to 1573 K in an Ar atmosphere of 70 mL/min.

Blends 1 and 2 were designed such that their basicity ratio (CaO/SiO$_2$) was adjusted to be 2 as shown in Table 2. The main purpose of Blend 1 was to enable the estimation of melt formation in the ordinary iron ore sinter mix. Blend 2 contained at least 2 wt% TiO$_2$. According to the phase diagram reported by Manshadi [1], this was sufficient to generate enough perovskite to be easily identified by XRD. The estimated chemical composition of selected compounds in the sinter blends is shown in Table 3, where the amount of TiO$_2$ in Blend 1 and Blend 2 was calculated to be 0.211 and 2.414 wt%, respectively.

**2.2. Experimental Procedure**

The temperature of melt formation in each sinter blend was estimated by measuring the heat flow in terms of differential scanning calorimetry (DSC) (TG-DSC, TGA/DSC 1 Star system Mettler Toledo (Mettler Toledo AG, Schwerzenbach, Switzerland). About 100 mg of each sinter blend was placed in an alumina crucible (7 mm ID × 8 mm OD × 4.5 mm height) and charged into the TG-DSC furnace. Temperature was non-isothermally raised at a rate of 20 K/min from 298 to 1573 K in an Ar atmosphere of 70 mL/min.

In an attempt to determine the temperature range at which more perovskite might form, sinter Blend 2 was mixed using the Turbula Mixer (T$_2$F Nr. Glen Mills Inc., Clifton, NJ, USA) at 34 rpm for one hour.
and pelletized into cylindrical pellets (6 mm diameter × 6 mm height) by being pressed at 20 MPa using a hydraulic work press. A vertical tube furnace was employed in the sintering experiments by raising the temperature by 20 K/min to a target temperature ranging from 1373 to 1523 K. The pellets were sintered by holding them at that specific target temperature for 1 h in 1 L/min gaseous atmosphere adopted from Hsieh et al. [11] of 75 vol% \( N_2 \), 24 vol% \( CO_2 \), and 1 vol% \( CO \) during the heating and holding stage. The pellet were pulled out to the cold end of the furnace and cooled to room temperature in 1 L/min air. The different sinter zones were simulated by changing the temperature to which the pellets from sinter Blend 2 were exposed during the holding time. In the actual sinter bed, different sinter zones are exposed to different oxygen partial potential due to the difference in temperature and the burning of coal. The oxygen partial pressures to which samples in this experiment were exposed are shown in Table 4.

### Table 4. Oxygen partial pressures to which the pellets from Blend 2 were exposed during sintering.

| Temperature (K) | CO/CO\(_2\) \( P_{O_2} \) (atm) |
|----------------|----------------------------------|
| 1373           | \( 2.7 \times 10^{-10} \)       |
| 1423           | \( 1.5 \times 10^{-9} \)        |
| 1473           | \( 7.8 \times 10^{-9} \)        |
| 1523           | \( 3.5 \times 10^{-8} \)        |

The oxygen partial pressures were evaluated using the thermodynamic data [12] below:

\[
3\text{Fe}_2\text{O}_3(s) + \text{CO}(g) = 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g) \tag{1}
\]
\[
\Delta G^\circ = -43,100 - 51.16T \text{ J/mol} \tag{2}
\]
\[
\text{Fe}_3\text{O}_4(s) + \text{CO}(g) = 3\text{FeO}(s) + \text{CO}_2(g) \tag{3}
\]
\[
\Delta G^\circ = 29,200 - 26.26T \text{ J/mol} \tag{4}
\]
\[
\text{CO}(g) + \frac{1}{2}\text{O}_2(g) = \text{CO}_2(g) \tag{5}
\]
\[
\Delta G^\circ = -281,900 + 87.34T \text{ J/mol} \tag{6}
\]

Equation (5) will govern the actual oxygen partial pressure in the furnace. The partial oxygen pressure at each temperature was suitable enough to allow for the reduction of hematite, but not for that of magnetite. After sintering, the cooled pellets were crushed for XRD analysis, and others mounted and prepared for point chemical composition as well as element distribution analyses using the EDS (Joel (Japan)/JSM-7100F, JEOL Ltd., Tokyo, Japan) and EPMA (Joel (Japan)/JXA-8530F, JEOL Ltd., Tokyo, Japan). The elemental mapping and point chemical analyses were done at 20 keV using 50 nA beam in the EPMA and in the EDS.

3. Results

3.1. Change in Morphology of Sintered Blend with Increasing Temperature

The morphology of sintered Blend 2 was investigated using an optical microscope (Leica DM 4000M, LEICA, Wetzlar, Germany) (Figure 2a–d).

The results clearly showed that the pellets sintered at 1473 K and below generated a lower amount of bonding materials, which might mean that low temperature sintering might result in poor sinter strength due to the availability of the low amount of bonding material. Thus, it is necessary to investigate the increased formation of melt at low temperatures by using materials such as \( B_2O_3 \). Increase in the sintering temperature to 1523 K generated more bonding phase, but most of the Ti was reported to be in the glass phase at high temperature, which might also affect the sinter strength due
the negative effects of Ti on the glass fracture toughness [3]. To verify the location of Ti in sintered Blend 2, XRD, EDS, and EPMA analyses were carried out on the sintered Blend 2.

3.2. Effect of Ilmenite on the Temperature of Melt Formation

The temperatures of melt formation in Blend 1 and Blend 2 were estimated using heat flow in the DSC. The typical DSC curves of Blends 1 and 2 shown in Figure 3 indicated some common change in the curve profile between 600 and 700 K, which might be attributed to the dehydration of the ores.

![Figure 3. Typical DSC curves of Blends 1 and 2 in an Ar atmosphere.](image)

It is believed that the first bonding phase to be formed might be calcium ferrites by solid-state reaction [13] since the basicity (CaO/SiO$_2$) of the sinter blends was fixed at 2. The melting temperature of calcium ferrite was estimated to be around 1473 K [13]. Melting is an endothermic process and a closer investigation of the DSC curve of Blend 1 shows some troughs around or near 1473 K, as shown in Figure 3. Accordingly, the temperature of melt formation in the sinter blends were estimated as shown in Figure 4.
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The temperature of melt formation in sinter Blend 1 was estimated to be around 1462 K, which is close to that predicted from the phase diagrams of CaO-SiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} and CaO-Al\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3}, which showed that the presence of a small amount of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} decreased the melting temperature of the first melt in high grade hematite sinter to the range of 1448 K to 1465 K [13]. In addition, the temperature of melt formation in Blend 2 was estimated to be 1550 K, as shown in Figure 4, which shows that the addition of ilmenite increased the melting temperature of the sinter blend. The increase in the temperature of melt formation may have been caused by the increase in Fe\textsubscript{3}O\textsubscript{4}(s) and TiO\textsubscript{2}(s) content in sinter Blend 2 that originated from the ilmenite ore. The low amount of bonding phases generated at low temperature in Figure 2a–c might have been because the temperature to which these sinters were exposed to was below the melt formation temperature of this blend, hence only bonding phases formed by the solid-state reaction were available in these sinters. Sintering Blend 2 at 1523 K improved the generation of the bonding phase because these phases might have developed both from the solid-state as well as from the partial melt since 1523 K is near the melt formation temperature of Blend 2, as shown in Figure 2d.

### 3.3. Effect of Temperature on the Change in Phase of Sintered Blend 2

The pellets prepared from Blend 2 were sintered in the temperature range of 1373 to 1523 K in a gas mixture of 1 L/min (75 vol% N\textsubscript{2}–24 vol% CO\textsubscript{2}–1 vol% CO) and then cooled down in air in order to identify the stable phases formed after sintering Blend 2 for 1 h.

Figure 5a shows that the major phases in the sinter are Fe\textsubscript{2}O\textsubscript{3}(s) (ICDD 00-0130534), MgO·Fe\textsubscript{2}O\textsubscript{3}(s) (ICDD 00-036-0398), and 3CaO·Fe\textsubscript{2}O\textsubscript{3}·TiO\textsubscript{2}(s) (ICDD 00-030-0259). The titanium existed in the calcium ferrite phase. MgO·Fe\textsubscript{2}O\textsubscript{3}(s) might have been from the substitution of Mg\textsuperscript{2+} for Fe\textsuperscript{2+} in the Fe\textsubscript{3}O\textsubscript{4}(s) since the ionic radii of Mg\textsuperscript{2+} and Fe\textsuperscript{2+} are comparable [14].
As shown in Figure 5b, the increase in the temperature to 1423 K resulted in the formation of CaO-Fe2O3(s) (ICDD 00-003-0804), MgO-Fe2O3(s) (ICDD 01-073-1720), FeO-Fe3O4-SiO2(s) (ICDD 00-052-1142), and CaO-TiO2(s) (ICDD 00-022-0153) phases. CaO-TiO2(s) was identified at the same peak position as CaO-Fe2O3(s) and Fe2O3(s). The increase in temperature might have provided enough energy for the detachment of TiO2(s) from FeO-TiO2(s), which resulted in the formation of perovskite.

At 1473 K, as shown in Figure 5c, CaO-TiO2(s) (ICDD 00-022-0153), MgO-Fe2O3(s) (ICDD 00-036-0398), and FeO-CaO-SiO2(s) (ICDD 00-034-0098) phases were identified. Calcium ferrite could not be identified at this temperature, probably because the melting temperature of calcium ferrite was estimated to be near 1473 K, as shown in Figure 3 [13]. The CaO from the melt might have reacted with TiO2 released from the ilmenite phase to form more CaO-TiO2(s) [4].

Raising the temperature to 1523 K, as shown in Figure 5d, led to the formation of 3CaO-TiO2-FeO-3SiO2(s) (ICDD 00-047-1877) and Fe2O3-3TiO2(s) (ICDD 00-047-1777), in addition to the CaO-TiO2(s) (ICDD 00-042-0423) and MgO-Fe2O3(s) (ICDD 00-036-0398) phases. As previously mentioned, the melting temperature of Blend 2 was estimated to be around 1550 K, as shown in Figure 4. Since 1523 K is near the melting temperature of Blend 2, this might allow FeO-CaO-SiO2(s) to partially melt, so more SiO2 and CaO-TiO2 dissolved into the melt, leading to the formation of the 3CaO-TiO2-FeO-3SiO2(s) phase. In addition, the cooling of the sintered pellets in air increased the availability of O2(g), which might have oxidized the unreacted ilmenite during cooling led to the formation of Fe2O3-3TiO2(s). It appears that the formation of CaO-TiO2(s) increases with increasing temperature. However, more in-depth analyses in terms of EDS and EPMA are required in order to verify these findings.

EDS analysis was carried out on the mounted and polished specimen of the sintered Blend 2 to identify some of the phases developed and to figure out how they changed with increasing temperature. In evaluating the atomic weight percent at each selected point, carbon, gold, chlorine, potassium, and...
bromine content at the selected points were considered trace elements due to their negligible amount in the original ores, as shown in Tables 1 and 3.

Sintering Blend 2 at 1373 K showed that most of the Ti was likely to be in the SFCA and in the Mg-enriched SFCA, as shown by Point 2 in the EDS results in Figure 6a and Table 5. There was also a great possibility of the formation of the calcium ferrite aluminate phase rich in Ti with large Al content. Large amounts of Ti were found in the Mg-enriched calcium ferrite aluminate phase as shown by Point 9 in Figure 6a and Table 5. More research must be done to further investigate this finding. The calcium ferrite aluminate phase (CFA) was reported to be an intermediate phase in the formation of SFCA [15]. The XRD analyses results shown in Figure 5a indicated that the Ti was likely to be in the calcium ferrite phase. The SFCA is a derivative of the calcium ferrite, hence the XRD results are in agreement with the EDS results, which showed that at this temperature, Ti is likely to be trapped inside the phases rich in Fe. V was also distributed in the Fe-enriched phase at this temperature; however, more results by EPMA are needed for further verification.

![Figure 6. EDS point analyses of sintered Blend 2 with increasing temperature: (a) 1373 K; (b) 1423 K; (c) 1473 K; and (d) 1523 K.](image)

**Table 5.** EDS analysis for Blend 2 sintered at 1373 K.

| Point | Atomic (%) |
|-------|------------|
|       | Fe | Ca | Si | Al | Ti | V | Mg | O   |
| 1     | 0.34 | – | 0.45 | 40.40 | – | – | – | 58.81 |
| 2     | 25.30 | 0.12 | 0.16 | 0.38 | 13.17 | – | 1.30 | 59.56 |
| 3     | 5.76 | 0.41 | 0.54 | – | – | – | – | 93.29 |
| 4     | 40.13 | 0.71 | 0.22 | 1.77 | 0.70 | 0.24 | – | 56.23 |
| 5     | 43.06 | 0.93 | 1.67 | 0.47 | 0.24 | – | – | 53.62 |
| 6     | 39.05 | 0.75 | 0.29 | – | 0.14 | – | – | 59.77 |
| 7     | 7.58 | 0.42 | 0.54 | 25.50 | 3.22 | – | – | 62.74 |
| 8     | 1.98 | 1.30 | 1.76 | 34.36 | 0.06 | – | – | 60.54 |
| 9     | 14.65 | 1.37 | 0.17 | 30.34 | 10.77 | – | 1.03 | 41.68 |
| 10    | 6.50 | 3.83 | – | 40.63 | – | – | – | 49.03 |

Increasing the sintering temperature of Blend 2 to 1423 K showed that most of the bonding phases were composed of Ti-enriched SFCA, Mg-enriched SFCA with small amounts of Ti and iron calcium.
silicate, as shown in Figure 6b and Table 6. Vanadium was also in the Ti-enriched SFCA. The XRD analyses shown in Figure 5b indicated that CaO-TiO$_2$(s) was identified in the Fe-enriched phases such as Fe$_2$O$_3$(s) and CaO-Fe$_2$O$_3$(s). The MgO-Fe$_2$O$_3$(s) whose peak was also identified at the same peak position as CaO-Fe$_2$O$_3$(s) might verify the presence of the Mg-enriched SFCA.

### Table 6. EDS analysis for sinter Blend 2 sintered at 1423 K.

| Point | Atomic (%) |
|-------|------------|
|       | Fe Ca Si Al Ti V Mg O  |
| 1     | 41.03 0.22 0.19 1.11 0.40 – – 57.04 |
| 2     | 28.40 1.59 1.03 1.59 0.37 – – 67.01 |
| 3     | 24.10 8.99 4.28 1.69 3.52 0.28 – – 57.15 |
| 4     | 83.63 2.54 0.81 0.27 1.88 – – 10.87 |
| 5     | 0.45 1.10 0.63 0.33 0.09 – – 97.40 |
| 6     | 9.78 1.07 11.92 – – – – 77.22 |
| 7     | 41.85 0.17 0.47 0.30 1.19 – – 56.01 |
| 8     | 36.08 0.39 0.30 0.50 0.19 – 3.39 59.15 |
| 9     | 39.33 0.04 0.05 0.05 0.04 – – 60.58 |
| 10    | 39.23 0.39 0.30 0.50 0.19 – – 65.33 |

Most of the Ti existed in the phases of iron calcium silicate and iron calcium aluminate in Blend 2 sintered at 1473 K, as shown in Figure 6c and Table 7. This might show that the Ti was distributed in the glass phase. Ti also existed in the phases of SFCA and Mg-enriched SFCA. The XRD results in Figure 5c show the presence of CaO-TiO$_2$(s) as an independent peak as well as in the same position as FeO-CaO-SiO$_2$(s) and Fe$_2$O$_3$(s). The presence of CaO-TiO$_2$(s) in the same position as FeO-CaO-SiO$_2$(s) might provide evidence that Ti was enriched in the glass phase.

### Table 7. EDS analysis for sinter Blend 2 sintered at 1473 K.

| Point | Atomic (%) |
|-------|------------|
|       | Fe Ca Si Al Ti V P S Mg O  |
| 1     | 58.85 3.86 0.68 – 2.12 – – – – 34.49 |
| 2     | 41.78 0.78 0.26 – 1.09 – – – – 56.09 |
| 3     | 39.31 0.29 – 1.47 1.69 0.19 – – – 57.05 |
| 4     | 9.46 15.08 8.73 0.23 0.38 – 0.79 – – 65.33 |
| 5     | 40.90 0.76 0.50 2.11 0.54 – – – – 55.19 |
| 6     | 32.52 4.93 4.49 1.57 0.51 – – – 1.18 54.79 |
| 7     | 34.31 0.09 – 0.63 0.44 – – – – 64.53 |
| 8     | 43.58 0.18 0.41 0.41 0.16 – – – 55.26 |
| 9     | 31.25 1.46 3.23 0.53 0.20 – – 0.27 – 63.16 |
| 10    | 24.00 5.77 1.09 1.25 4.93 – – – – 62.97 |

Finally, at 1523 K, most of the Ti existed in the iron calcium aluminate phase, and some of the Ti was in the phases of iron calcium silicate as well as SFCA, as shown in Figure 6d and Table 8. The XRD results in Figure 5d show the presence of the 3CaO-TiO$_2$-FeO-3SiO$_2$(s) phase. The EDS results seem to show that more Ti was likely to be in the glass phase with an increase in temperature.
Table 8. EDS analyses for Blend 2 sintered at 1523 K.

| Point | Fe  | Ca  | Si  | Al  | Ti  | V  | P  | S  | Mg | O   |
|-------|-----|-----|-----|-----|-----|----|----|----|----|-----|
| 1     | 34.51 | 0.15 | –  | 0.51 | 0.48 | –  | –  | –  | –  | 64.34 |
| 2     | 1.78  | 20.43 | 11.49 | –   | –   | –  | 0.36 | –  | 0.26 | 65.67 |
| 3     | 6.65  | 15.24 | 13.79 | 0.33 | –   | –  | 0.20 | –  | 0.42 | 63.35 |
| 4     | 38.14 | –    | –   | –   | –   | –  | –  | –  | –  | 61.87 |
| 5     | 33.48 | 7.17 | 4.53 | 0.46 | 1.10 | –  | –  | –  | –  | 53.26 |
| 6     | 4.15  | 20.58 | 9.70 | 0.23 | 0.211 | –  | –  | –  | –  | 65.13 |
| 7     | 33.60 | 0.12 | –   | 0.48 | 0.50 | –  | –  | –  | –  | 65.29 |
| 8     | 40.61 | 0.13 | –   | –   | –   | –  | –  | –  | –  | 59.24 |
| 9     | 33.03 | 0.33 | –   | 1.41 | 1.25 | –  | –  | –  | –  | 63.98 |
| 10    | 4.57  | 16.87 | 12.63 | 0.23 | –   | –  | 0.59 | –  | 0.94 | 64.18 |
| 11    | 31.57 | 0.40 | –   | 2.59 | 1.88 | –  | –  | –  | –  | 63.57 |

3.4. Effect of Temperature on Elemental Distribution in the Sintered Blend 2

To validate the XRD results, EPMA analyses were performed for the sintered and polished specimen of Blend 2 sintered in 75 vol% N_2, 24 vol% CO_2, 1 vol% CO in the temperature range of 1373 to 1523 K and cooled in air. According to the mapping of elemental distribution, titanium and other metallic elements in the sinter Blend 2 were distributed as shown in Figure 7a–d.

Figure 7a shows that part of the Ti was distributed in the same region as Fe and Ca, which is in good agreement with the XRD results shown in Figure 5a that showed the presence of 3CaO·Fe_2O_3·TiO_2(s). The EDS results indicate that the Ti was most likely to be in the Mg-enriched SFCA and Mg-enriched FCA phase at this temperature.
Figure 7b shows some areas with increased interaction between Ca and Ti. These areas had some Fe. This might show that CaO·TiO₂(s) with a small amount of Fe was formed. The XRD results showed the presence of CaO·TiO₂(s) at the same peak position as the Fe-enriched phases, Fe₂O₃(s) and CaO·Fe₂O₃(s). Some regions had Fe and Ca distributed in the same area, which might indicate the CaO·Fe₂O₃(s) phase identified by XRD. EDS showed that most of the Ti was in the SFCA at this temperature.

Figure 7c shows that more Ti existed in the same area as Ca, showing the possibility of forming more CaO·TiO₂(s), and these areas contained some Fe at 1473 K. EDS showed that Ti existed in the phases of iron calcium silicate and iron calcium aluminate. Fe, Ca, and Si existed in the same area, showing the possibility of the existence of the FeO·CaO·SiO₂(s) identified by XRD in Figure 5c. The presence of Mg in the same region as the Fe-enriched region showed the possibility of Mg²⁺ replacing Fe²⁺ ions in the Fe₃O₄(s) crystal structure, leading to the formation of Mg-enriched SFCA as shown by EDS. Vanadium was also in the Fe-rich phase, which is in agreement with the EDS results at Point 3 shown in Figure 6c and Table 7.

At 1523 K (Figure 7d), titanium (Ti), vanadium (V), and aluminum (Al) were concentrated in the same region. These areas had some Fe. EDS showed that Ti existed in the iron calcium aluminate phase, and some of the Ti was in the iron calcium silicate as well as in the SFCA. XRD showed the possibility of the existence of the 3CaO·TiO₂·FeO·3SiO₂(s) phase. Si was found to be in the Ca-enriched area, and in some points along with Mg. This shows the possibility of the existence of the magnesium calcium silicate phase at Point 2 in the EDS results (Figure 6d and Table 8) in Blend 2 sintered at 1523 K.

4. Discussion

Based on the XRD data, the phase of perovskite in sintered Blend 2 was quantified, and the results are shown in Figure 8. The results showed that the formation of perovskite might increase with an increase in temperature up to 1473 K, and decrease at 1523 K. Part of the Ti was in the 3CaO·TiO₂·FeO·3SiO₂ and the Fe₂O₃·3TiO₂ in the sinter blend sintered at 1523 K as shown in Figure 8. This decreased the amount of perovskite formed, but Ti was in the glass phase, which might affect the sinter strength.

![Quantified perovskite content from the XRD phase analyses data.](image)

The low temperature sintering technique might limit the formation of perovskite in this sinter, but the formation of the small amount of melt shown in Figure 2a,b might result in the availability of a smaller amount of bonding phase. Furthermore, the effect of increasing Ti in the SFCA structure on sinter bonding strength should also be fully explored and understood. Increasing the sintering temperature to above 1473 K resulted in the melting of CaO·Fe₂O₃, generating more CaO·TiO₂ from...
the reaction between TiO₂ and CaO in the molten CaO·Fe₂O₃. At much higher temperatures of about 1523 K, the Ti was entrapped into the glass phase, which might weaken the sinter because of the negative effect of Ti on the glass phase fracture toughness [3].

Based on the XRD, EDS, and EPMA analysis results, the location of Ti with increasing temperature in this hematite–ilmenite ore sinter blend can be summarized as shown by Figure 9 below:

![Figure 9. Summary of the location of Ti with increasing temperature in the hematite–ilmenite ore sinter.](image)

To fully utilize Ti-containing ores, low temperature sintering with an additive like B₂O₃ should be investigated to generate more liquid phase in these sinters.

5. Conclusions

The sintering behavior of the hematite–ilmenite ore sinter blend was investigated based on the experimental results, and the following conclusions were obtained:

1. Addition of ilmenite ore to hematite ore increased the melt formation temperature of the sinter blend.
2. Addition of ilmenite ore to hematite ore resulted in the formation of more perovskite with increasing temperature up to 1473 K. More Ti was likely to exist in the glass phase with further increase in temperature.
3. Based on morphological analysis results, the amount of bonding phase formed increased with increasing temperature.
4. The low amount of bonding phase generated at low temperature might result in weak bonding strength and at elevated temperatures of over 1473 K; more Ti is likely to be distributed in the glass phase, which might affect the glass phase fracture toughness.
5. Ti existed in the Fe-enriched phase at low temperature since Ti was in the SFCA phase at 1423 K, and above this temperature, more Ti existed as CaO·TiO₂ and in the glass phase. Further research should be done to clarify the effect of MgO addition on this sinter, and on low temperature sintering by adding B₂O₃.

Author Contributions: Following an idea of S.-M.J. and E.K.C. Conceptualization by E.K.C. was followed by E.K.C. and S.-K.C. carrying out the experiments. E.K.C. evaluated the data and drew conclusions. Draft preparation and writing of manuscript was done by E.K.C. Supervision of the entire work was done by S.-M.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Wan Ju Kim for their help in the XRD analysis, Keun Chang Park in the EPMA operation, and Lee Sang Ryul for their help in gas calibration and preparation of the experimental samples. The authors would like to express their gratitude toward the anonymous reviewers whose comments improved this work.

Conflicts of Interest: The authors declare no conflict of interest.

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