**Sintering Characteristics of Titanium Containing Iron Ores**

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(Received on March 26, 2014; accepted on July 7, 2014)

The effect of Ti-oxide on the sintering behaviour of iron ore has been studied by doping pure TiO₂ to a sinter blend in laboratory tests. The results showed a considerable effect of TiO₂ on sinter strength, where the tumble index increased with increasing TiO₂% (up to 2.0%). However, doping more than 2.0% TiO₂ to the sinter blend decreased its strength. The melting point of the sinter was also affected by increasing the TiO₂ content, indicating a possible change in the coke consumption during industrial-scale sintering of Ti-bearing ores. Optical and electron microscopy studies of sinter structures confirmed a general improvement in the overall pore structure and sinter melt by increasing TiO₂ content of the sinter blend up to 2.0%. An important feature of the sinter structure was the observation of perovskite phase formation and an increase in the volume fraction of this phase obtained by increasing TiO₂. The formation of this perovskite phase was considered as an important reason for the reduction of the sinter melting point. Also, doping TiO₂ to the sinter mix resulted in stabilizing and increasing the volume fraction of the larnite phase in the sinter structure.

**KEY WORDS:** iron ore sintering; compact sintering; titanium oxide; perovskite; larnite.

1. Introduction

Titanium-bearing iron ores are found in many large deposits around the world and are becoming an important alternative source of iron ore due to the shortage of economic high purity ores. For instance, high titanium (and vanadium) magnetite concentrates account for more than 14% of China’s national iron ore resources. On the other hand, in many cases Ti-bearing secondary raw materials (containing TiO₂) are introduced into the blast furnace to protect the hearth and extend the blast furnace operating life. As the refractory material in the blast furnace hearth is the most critical part of the blast furnace, extending the life of this area can extend the operation life of the whole blast furnace. The mechanism by which the blast furnace hearth can be protected by addition of titanium to the burden is via the formation of complex titanium carbo-nitrides. These titanium carbo-nitrides with very high melting point form in the hot area of the blast furnace and then precipitate in the cooler area of the hearth, i.e. the area where the most heat is lost, as an additional refractory.

The titanium added to the blast furnace burden may also go through into the molten metal, forming Ti-containing steels at the end of the steel making process. Small additions of Ti to the steel can improve the mechanical properties of products through formation of nano-scale titanium nitride and carbo-nitrides. While some part of the Ti in the blast furnace burden forms a protective layer on the hearth refractory and a small part may remain in the molten metal, the majority of Ti partitions to the slag and forms a high Ti containing slag. Therefore, the effect of addition of Ti-bearing materials to the blast furnace on the behaviour and properties of slag is another important issue that should be considered when using those materials.

Based on the noted beneficial aspects associated with the addition of Ti to the blast furnace, a controlled amount of Ti-bearing ore should be added to the burden to effectively protect the refractory at the hearth, while maintaining smooth operation of the furnace. The amount of this Ti-bearing ore is very dependent on the type of the Ti-bearing ore as well as the condition of the hearth and typically falls between 4–7 kg/tonne of the hot metal.

A number of different titanium containing raw materials could be used as a source of titanium addition to the blast furnace burden. The main mineral sources of titanium are ilmenite and titano-magnetites, (Fe,Ti)O₃. Iron sand, which is a magnetite-iluvospinel solid solution, is the most important titania-magnetite ore type. The direct reduction of iron sand is very slow, needs high energy and has a narrow processing temperature window. Titaniferous magnetite ore is usually very fine and, therefore, added to the sinter mixture rather than a direct charge to the blast furnace. However, some types of Ti-containing fluxes such as Sorel flux, can be added directly to the blast furnace charge.

The first stage in studying the effect of addition of Ti-bearing materials to the blast furnace and its operation is to understand the influence of Ti on the sintering behaviour of iron ore fines. Although the exact influence of Ti addition on the sintering behaviour is yet to be cleared, there is a general agreement that increasing the Ti level in the sinter mix can reduce productivity and sinter strength and also negatively affect sinter reducibility. The Reduction Degradation Index (RDI) of sinter has also been found to be strongly correlated to the titanium content of the sinter.
hand, a considerable effect of titanium oxide on mineralogy, and consequently on strength, of sinter is expected.\textsuperscript{11) However, it is worth noting that both of the negative effects of Ti addition on sinter behaviour strongly depend on the type and composition of Ti-bearing raw material.

The sintering behaviour of titanium-bearing ores has been previously studied in several works.\textsuperscript{2, 9–11) However, as sintering behaviour is affected not only by the amount of Ti in the ore but also by the type and composition of ores, different behaviour has been reported so far, especially with respect to the structure and composition of sinter products. For instance, while Paananen\textsuperscript{3) showed no difference in the distribution of Ti in different sintered phases, Bristow and Loo\textsuperscript{2) claimed that most of the Ti added to the sinter blend will concentrate in the glass phase, with less concentration in magnetite, hematite or Silico-ferrite of Calcium and Aluminium (SFCA).

The aim of this work was to study the sole effect of titanium-oxide on sintering behaviour of iron ore. In this regard different amounts of pure TiO\textsubscript{2} were doped into an iron ore blend and the different sintering and morphological behaviours were studied.

2. Experiments

The iron ore used in this study was a high-grade hematite fine ore with chemical composition presented in Table 1. This ore was oven dried at 105°C for 24 hours and after screening, the –1 mm size fraction was chosen for sintering experiments (due to small volume of compact sinter blends using larger fines is not practical). Pulverized limestone and pure silica fluxes were used to adjust the basicity and SiO\textsubscript{2} levels of sinter blends to 1.8 and 5.0%, respectively. Analytical grade TiO\textsubscript{2} (99.5% TiO\textsubscript{2}) was doped in the sinter blend at levels of 0, 0.2, 0.5, 1.0, 2.0, 5.0, 7.0 and 10.0 wt%.

The ore, flux and TiO\textsubscript{2} were mixed and homogenized in a laboratory-scale mixer. Two compacted cylindrical tablets of the sinter blend were prepared and fired in a laboratory tube furnace using a standard heating profile and holding at different temperatures for 3 min. The furnace atmosphere was charged with an oxygen partial pressure of 5*10\textsuperscript{-3} atm. The details of the experimental facility are presented elsewhere.\textsuperscript{12) After sintering, the fired compacts were tumbled together for a duration of 8 min in a modified Bond Abrasion tester.\textsuperscript{12) Then, the tumbled particles were screened to measure the Tumble Index (TI) as the percentage retained above 2.0 mm.

For sinter mineralogy studies, repeated compact sintering experiments were performed for different TiO\textsubscript{2} doped fractions and firing temperatures. The sintered compacts were metallographically prepared by sectioning, mounting in cold resin, grinding and polishing up to 1 \(\mu\)m diamond paste. Then the microstructures were studied using optical and scanning electron microscopy (SEM). The composition of phases of interest was studied using energy dispersive X-ray spectrometry (EDAX) in SEM as well as electron probe micro-analyser (EPMA).

### Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>P</th>
<th>CaO</th>
<th>TiO\textsubscript{2}</th>
<th>Mn</th>
</tr>
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<tbody>
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<td>Wt%</td>
<td>65.14</td>
<td>1.66</td>
<td>1.35</td>
<td>0.04</td>
<td>0.08</td>
<td>0.04</td>
<td>0.69</td>
</tr>
</tbody>
</table>

3. Results

3.1. Effect of TiO\textsubscript{2} Doping on Sinter Strength

One of the principal requirements for every sintering process is good sinter strength to avoid the disintegration of the sinter material in the upper part of the blast furnace and, hence, to optimise the permeability of the furnace charge. To study the strength of sinter with different TiO\textsubscript{2} contents, the compact strength (TI test) of different sinter mixtures was measured and plotted as a function of sintering temperature (Fig. 1). It is clear that in all sample mixtures the sinter strength increased with increasing temperature and reached a maximum value of above 80% TI. The temperature where 80% TI was obtained was considered as the optimum melting point of the sinter mixture.\textsuperscript{12) This melting point, in fact, is a temperature where enough fraction of sinter blend could melt and then able to hold all sinter blend together after solidification. According to ISO-3271 standard,\textsuperscript{13) this characteristic of melting point (i.e. holding all sinter blend together) confirm by measuring the tumble strength of sinter product. The laboratory experiments have shown that 80% plus 2.0 mm in the current compact sintering set up is equivalent to ISO tumble index of 62% plus 6.3 mm in standard pot grate sinter.\textsuperscript{12) Surprisingly, increasing the amount of TiO\textsubscript{2} in the sinter mixture up to 2.0% reduced the melting point, after which melting point started to increase again.

![Figure 1](attachment:image1.png)

**Fig. 1.** Compact TI of sinter blends with different doped TiO\textsubscript{2} levels as a function of firing temperature.

![Figure 2](attachment:image2.png)

**Fig. 2.** Melting temperature of sinter blend as a function of doped TiO\textsubscript{2} % level.
shows such change in the melting point by doping the sinter mixture with TiO\(_2\). As the melting point is somehow representative of the fuel consumption during the sintering process, doping pure TiO\(_2\) is expected to reduce the coke consumption (at least up to 2.0% TiO\(_2\)). However, it should be noted that most of the literature confirmed that adding Ti-bearing ores to sinter blends had no or limited influence on coke consumption in industrial sintering.\(^{2}\)

To evaluate the effect of doping pure TiO\(_2\) on sintering behaviour and sinter mineralogical characteristics, microstructural analysis was performed on TiO\(_2\) doped sinters using optical and electron microscopy.

3.2. Effect of TiO\(_2\) Doping on Sinter Microstructure

a) Sinter Matrix Pore Structure

Figure 3 shows the general sinter structure of blends with different amounts of doped TiO\(_2\) after firing at different temperatures. A detailed assessment of this figure indicates the clear influence of TiO\(_2\) addition on sinter structure development. In the sinter blend with no added TiO\(_2\), the sinter didn’t fully melt and no significant consolidation was observed at the relatively low temperature of 1260°C (Fig. 3(a)). When the firing temperature was increased to 1270°C, the sinter started to melt, but the pores remained generally irregular in shape, indicating incomplete melting. This structure also includes some relatively large and un-reacted hematite particles (Fig. 3(b)). When the temperature increased to 1280°C, a higher portion of the sinter blend melted and its structure shows a large number of well-rounded pores along with a small fraction of irregular pores. This sinter structure (Fig. 3(c)) indicated that while sintering was good at this firing temperature, complete melting had still not occurred. However, the TI test results showed a maximum strength (i.e. 80% + 2 mm) at this temperature. The melting process of the sinter blend was complete at 1290°C and the sinter structure at this temperature shows a very well melted and consolidated sinter structure (Fig. 3(d)).

When the sinter blend was doped with 0.5% TiO\(_2\), the structure started to show deviation from the previous sinter blend (Figs. 3(e)–3(h)). After firing at 1260°C, limited melting occurred in the sinter mixture and large and irregular pores, as well as a high fraction of un-reacted hematite were present, whereas the sinter started to melt completely after firing at 1270°C. At this temperature a more melted sinter structure is visible compared with the same temperature in the sample with no added TiO\(_2\). A fully melted structure was obtained after firing at 1280°C, but over-melting occurred when the firing temperature was increased to 1290°C (Fig. 3(h)). A comparison between Figs. 3(a)–3(d) and 3(e)–3(h) indicates that doping the sinter mixture with TiO\(_2\) reduced the melting point in the sinter blend, which supports the TI test results in Fig. 1.

It can be seen that by increasing the doped TiO\(_2\) fraction to 2.0% (Figs. 3(i)–3(l)), the influence of TiO\(_2\) on sinter pore...
structure was very different, compared with samples doped to lower TiO$_2$ levels. At the 2% TiO$_2$ level, the initial melting temperature was reduced to 1260°C. In this case, a consolidated structure, with limited numbers of irregular pores and un-reacted hematite grains, was observed after firing at 1260°C. The melting was completed by increasing the firing temperature to 1270°C, where a fully melted structure, with all pores well-rounded and negligible un-reacted hematite was observed in the sinter structure. Increasing the firing temperature in this sample to 1280°C resulted in an over-melted sinter structure with a uniform and fine-grained sinter matrix full of smooth-walled pores (Fig. 3(k)).

Increasing the TiO$_2$ content beyond 2.0%, the sinter structure started to shift to similar structures as in the low TiO$_2$ samples. For instance when doping the sinter mixture with 10% TiO$_2$, a structure with a high fraction of irregular shape pores, un-reacted hematite and a low volume of sinter melt was obtained after firing at 1260 and 1270°C. When increasing the firing temperature to 1280 and then 1290°C, however, the sinter blend melted and more rounded pores with less un-reacted hematite were obtained, although little loss of volume occurred even at 1290°C.

An overview of Fig. 3 indicates that doping with a small amount of TiO$_2$ may improve the sintering process by reducing the melting point, improving the sinter structure and enhancing strength. However over-doping (more than 2.0% TiO$_2$) can have negative effects on the sinter properties.

b) Sinter Mineralogy

Sinter structures formed in different samples were examined using optical and scanning electron microscopy to evaluate the phase development of sinter at different temperatures and TiO$_2$ contents. The investigations were concentrated on sinter formed at or close to the optimum Ti temperatures. The sinter matrix in most of the blends was generally composed of SFCA, hematite and magnetite, as well as some lamite (Ca$_2$SiO$_4$) and Ti-rich perovskite. Both sintering temperature and TiO$_2$ addition significantly affected the development of such phases during sintering. While increasing temperature (for a given TiO$_2$ addition) caused formation of more magnetite, secondary hematite (which formed from melt solidification) and SFCA, increasing TiO$_2$ up to 2.0% (for a given sintering temperature) showed a similar influence.

3.3. Formation of Perovskite Phase in the Sinter Structure

Solidification and crystallization of sinter melt containing a high fraction of TiO$_2$ will create different phases and compositions compared with low TiO$_2$ sinter blends. As there is no suitable mineral in which TiO$_2$ can substitute during crystallization of the sinter melt, TiO$_2$ tends to form its own mineral phase. As there is a high fraction of Ca in the sinter blend, perovskite (CaTiO$_3$) could be a suitable phase for TiO$_2$ to crystallize in. The presence of the perovskite phase was observed in many samples using electron micro probe analysis, SEM studies, Energy Dispersive X-ray Spectroscopy (EDX) analysis as well as XRD studies (Fig. 4).

3.4. Distribution of Ti in the Sinter Matrix

The distribution of titanium in different phases of the sinter may be considered as an important factor of its influence.

Fig. 4. a) and b) Perovskite phase in 2.0% TiO$_2$ sinter blend after firing at 1280°C, c) XRD pattern of sinter structure containing perovskite (P).
on sinter strength and structure. Previous research has reached very different observations on the melting behaviour of Ti-bearing iron ores during sintering and the subsequent distribution of Ti in different phases of sinter structure. While Paananen et al.\textsuperscript{3)} indicated that TiO\textsubscript{2} was distributed uniformly in the sinter structure, Bristow and Loo\textsuperscript{2)} found that most of the added TiO\textsubscript{2} will segregate to the glass phase, with less concentration in the hematite and magnetite phases. To understand the distribution of TiO\textsubscript{2} in different sinter phases in this study, some SEM EDX analysis was performed for different phases. The results of such measurements showed negligible Ti in hematite and magnetite phases, with the majority of the Ti distributed between perovskite and SFCA phases. \textbf{Figure 5} shows an example of the difference in distribution of Ti in different phases including hematite, SFCA and perovskite. It is clear that most of the Ti was distributed in perovskite and SFCA phases with very limited, if any, occurrence in hematite. Many other measurements of Ti content in different sinter phases using SEM and/or EPMA showed very similar results confirming the distribution of most Ti in the perovskite and SFCA phases.

\section*{4. Discussion}

An increase in the level of TiO\textsubscript{2} doping in the sinter blend caused deterioration in the sinter structure, melting point and sinter strength. When the TiO\textsubscript{2} level increased from zero to 2.0\%, the melting point of the sinter was reduced by more than 25°C. This indicates that a possible reduction in the coke consumption in an industrial sintering plant could be achieved by increasing the TiO\textsubscript{2} to the sinter blend. However, the melting point started to increase when doping the blend with more than 2.0\% TiO\textsubscript{2}. Such reduction in the melting point by increasing TiO\textsubscript{2}%, at low level, could be attributed to the influence of TiO\textsubscript{2} on different phase development as well as formation of new phases (perovskite) during the sintering process. To evaluate the effect of TiO\textsubscript{2} addition on reducing the melting point of the sinter mixture through the formation of perovskite, the CaO–TiO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3} phase diagram has been employed. \textbf{Figure 6} shows a projection of the liquidus surface of the ternary phase diagram.\textsuperscript{14)} This diagram clearly shows that addition of TiO\textsubscript{2} to the sinter mixture (i.e. iron-oxide and CaO) can produce perovskite within a wide range of mixtures. The perovskite, in conjunction with other phases in the diagram, can produce several liquidus points with relatively low melting temperatures. Two of the most important liquidus points are shown as \textit{A} and \textit{B} in Fig. 6. Point \textit{A} is a phase assembly of perovskite, calcium-ferrite (CF) and hematite with a liquidus temperature of 1220°C. Also, point \textit{B} is a phase assembly of perovskite, calcium-ferrite and dicalcium-ferrite (C\textsubscript{2}F) with a liquidus temperature of 1223°C. The presence of such phase assemblies with low melting points can explain the reduction in the melting point of sinter mixtures doped with TiO\textsubscript{2}. In fact, when those low temperature phases form within the sinter matrix they will melt at lower temperatures in compared with other area of sinter mix, and then reduce overall melting temperature of sinter blend. However, such low temperature phase assemblies are presented at low TiO\textsubscript{2} fractions, and as shown by the arrow in Fig. 6, increasing the TiO\textsubscript{2} level beyond the equilibrium fraction of those liquidus points will increase the melting point (similar to what we observed after doping more than 2.0\% TiO\textsubscript{2} in the sinter mixture (Fig. 2)). Although this diagram cannot exactly represent the current sintering conditions (as silica and alumina are not included, and also represents study under an air atmosphere rather than at the lower oxygen partial pressure of 5*10\textsuperscript{-3} atm in
the current work), it is still possible to interpret the potential effect of TiO2 addition on the liquidus temperature. According to this diagram, the low liquidus points occur at around 2–3% TiO2 and any increase or decrease from this level will increase the liquidus temperature, which is compatible with the findings in this study.

The abovementioned lowering in the melting point (when doping with TiO2) influenced the sinter strength (as seen in Fig. 1). The effect of TiO2 addition on the sinter strength is somewhat in contrast with previous research. The key to such unexpected results can be traced in the difference between TiO2 doped sinter mixtures and high Ti ores. For instance, Bristow and Loo have shown that addition of iron sand (as a high-Ti iron ore with 7.7% TiO2) to a sinter blend increased the tumble strength (TI) of the sinter and always kept the strength towards the upper range of the target (which was 62 ± 2% pot grate TI). They related such improvement in the sinter strength to the oxidation of the titanomagnetite during the sintering process, hence increasing the level of secondary hematite and SFCA phase.

Another important piece of evidence for lowering the melting point of sinter by doping with TiO2 is the formation of a secondary skeletal hematite phase in the sinter structure. This skeletal hematite phase was a common phase formed in many high TiO2 content blends. While the skeletal hematite is only expected at high sintering temperatures (such as those found during pot grate sintering with firing temperatures of above 1300°C), a relatively high fraction of this phase was observed in sintered from the highly doped mixtures (TiO2 > 1.0%) used in some of our compact sintering experiments (Fig. 7). Studies have shown that this secondary skeletal hematite could have a very detrimental effect on RDI.

One of the important microstructural features observed during this study was the formation of larnite and the increase in the volume fraction of this phase when doping more TiO2 to the sinter blend. Larnite is a β-calcium orthosilicate (\(\beta-Ca_2SiO_4\)) with a monoclinic structure and has long been known to occur in iron ore sinter. With its lenticular shape and characteristic occurrence at hematite/magnetite grain boundaries, as well as its high solubility in water, larnite is known as a potentially deleterious phase for mechanical properties of sinter. Our microstructural studies using SEM and optical microscopy revealed the presence of a considerable volume of larnite in high TiO2 samples sintered at temperatures above 1280°C. Figure 8 shows the microstructure of a blend containing 1.0% TiO2 sintered at 1290°C, indicating the presence of a large fraction of larnite phase. It has been shown that larnite is thermodynamically unstable below 675°C and can invert to a stable phase of \(\gamma-Ca_2SiO_4\). Then, it is expected that if larnite forms in the sinter melt, it can invert to \(\gamma-Ca_2SiO_4\) (known as Calsio-Olivine) during cooling of the sinter. Such an inversion is accompanied by a large volume change of almost 10% from 345.2 Å\(^3\) (larnite) to 384.2 Å\(^3\) (\(\gamma-Ca_2SiO_4\)). Such a volume change could be enough to cause breakdown of the sinter and produce fine powder in a sinter structure with high volume fraction of larnite. However, the observation of a large fraction of larnite phase in the compact sinter doped with high TiO2 in the current study (Fig. 8) indicates that such inversion didn’t happen and larnite phase remained stable as a constituent phase of sinter to the room temperature. A distinct feature of larnite that we observed during sample preparation was high reactivity of this phase to the water and most of this lenticular phase washed out during sample polishing (when water based polishing solution used). This feature didn’t let us to use normal water based solutions for sample polishing and we had to move to ethanol based solutions. Such feature confirms that larnite conversion to the calsio-olivine didn’t happen (calsio-olivine can dissolve in water at temperatures above 200°C) and the lenticular phase observed in the sinter structures is still larnite.

Previous studies have shown that addition of some oxides to the sinter blend (such as P2O5 and V2O5) can prevent the inversion of larnite to the \(\gamma\) phase and stabilize larnite up to the room temperature. Also, the presence of silicate in the sinter melt could have a similar effect and can stabilize the larnite. Considering this, it could be concluded that the presence of TiO2 can not only encourage the formation of larnite (probably by delaying SFCA formation and then leaving more Ca available to form larnite in the later stages of sinter melt solidification), it might also have a similar ability to that of P2O5, the presence of which is considered to help sta-
bilise the larnite in the sinter structure. To confirm the similar effect of TiO$_2$ on stabilizing the larnite as P$_2$O$_5$ and V$_2$O$_5$, the micro-probe analysis was performed on several larnite particles and the presence of 0.18–0.25% Ti was confirmed in larnite. This data is supportive of the ability of Ti-oxide to prevent the larnite inversion and thus reduce the harmful influence of larnite to calso-olivine inversion on the mechanical properties of the sinter. However, the lenticular shape and sharp edges characteristic of larnite, as well as its high water solubility, remain potentially detrimental to the sinter structure.

5. Conclusion
The effect of TiO$_2$ doping on the sintering behaviour of iron ore was studied using compact sintering technique. Doping TiO$_2$ into the compact sinter mix had considerable effects on sintering behaviour, properties and mineralogical characteristics of the final sinter product.

1. Addition of TiO$_2$ to the sinter mix produced significant effects to the sinter strength and mineralogy.
2. When the TiO$_2$ level increased from zero to 2.0%, the melting point (i.e. where 80% tumble index was obtained) of the sinter was reduced by more than 25°C.
3. Microstructural observations as well as thermodynamical expectation from phase diagram, confirmed that formation of perovskite (CaTiO$_3$) could be considered as an important factor in lowering the sinter melting point.
4. Addition of TiO$_2$ to the sinter increased the volume fraction of the larnite phase in the sinter structure by delaying formation of SFCA and then leaving more Ca available to form larnite in the later stages of sinter melt solidification. This TiO$_2$ doping also stabilized larnite to the room temperature by preventing the inversion of larnite to the calso-olivine ($\gamma$-Ca$_2$SiO$_4$).

Acknowledgments
The authors gratefully acknowledge the financial support of CSIRO to carry out this work and the improvements made to the manuscript made by internal and external reviewers. Abebe Haileslassie prepared the polished sections used for microscopic analysis.

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