Sintering Performance of Titanium Bearing Iron Ores

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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 shortage of high purity ores. More importantly, in many cases Ti-bearing secondary raw materials 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 then precipitate in the cooler area of the hearth, i.e. the area where the most heat is lost, as an additional refractory.

The amount of Ti-bearing ore added to the burden should be controlled to effectively protect the refractory at the hearth while maintaining smooth operation of the furnace. This is very dependent on the condition of the hearth and typically falls between 4-7 kg/tonne of the hot metal, usually added to the sinter mixture rather than as a direct charge to the blast furnace.

The sintering behaviour of titanium-bearing ores has been previously studied in several works [1-4]. 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 in the literature, especially with respect to the structure and composition of sinter products. For instance, while Paananen and Kinnunen [2] showed no difference in the distribution of Ti in different sintered phases, Bristow and Loo [1] claimed that most of the Ti added to the sinter blend will concentrate in glass, with less concentration in magnetite and hematite phases.

In the present work the specific effect of titanium oxide on sintering behaviour of iron ore has been studied by doping pure TiO$_2$ into a simulated sinter blend. In this regard, different fractions of analytical grade TiO$_2$ were doped to a sinter blend containing a high-grade hematite ore and sintering was performed under controlled laboratory conditions, using a compact sintering technique developed by CSIRO [5]. The sinter strength and its mineralogical characteristics were studied. To study the strength of sinter, fired compacts were tumbled together for a duration of 8 minutes in a modified Bond Abrasion tester [5]. Then, the tumbled particles were screened to measure the Tumble Index (TI) as the percentage retained above 2.0 mm. The TI values were plotted as a function of sinter temperature (Figure 1) and the temperature where the TI value first reached 80% TI was considered as the melting point of the sinter.

Results of this work showed the considerable effect of TiO$_2$ on sinter strength as well as on melting point. While doping TiO$_2$ up to 2.0% improved the sinter strength and reduced the melting point, any addition of TiO$_2$ beyond that point negatively affected sinter strength and melting point (Figure 2). Similarly, doping up to 2.0% pure TiO$_2$ to the sinter improved the sinter matrix pore structure and its mineralogy. Figure 3 shows some examples of the sinter...
structure of blends with three different TiO₂ levels after firing at 1270 °C, clearly showing increased consolidation (volume reduction) and melting with increasing TiO₂.

Figure 1: Compact TI of sinter blends doped to different TiO₂ levels (%)

Figure 2: Melting temperature of sinter blends doped to different TiO₂ levels

Figure 3: Sinter structure of blends with different TiO₂ levels after firing at 1270 °C

An important microstructural feature of sintering with high TiO₂ compositions was formation of perovskite as a discrete phase in the sinter structure. Although some Ti can be taken up by other phases, not all is accommodated in this way. As there is a high fraction of Ca in the sinter blend, perovskite (CaTiO₃) is a possible discrete phase for TiO₂ to crystallize in. The presence of the perovskite phase was observed in many samples using a scanning electron microscope and Energy Dispersive X-ray Spectroscopy (EDX) analysis. This perovskite
phase formation could be contributing to the observed trend in the sinter melting point in TiO$_2$ doped blends (Figure 2).

To evaluate the effect of TiO$_2$ addition on the melting point of the sinter mixture through the formation of perovskite, the CaO-TiO$_2$-Fe$_2$O$_3$ phase diagram has been employed. Figure 4 shows a projection of the liquidus surface of the ternary phase diagram [6]. This diagram clearly shows that addition of TiO$_2$ 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 A and B in Figure 4. Point A is a phase assembly of perovskite, calcium-ferrite (CF) and hematite with a liquidus temperature of 1220 °C. Similarly, Point B is a phase assembly of perovskite, calcium-ferrite and dicalcium-ferrite (C$_2$F) with a liquidus temperature of 1223 °C. The presence of such phase assemblies with low melting points may explain the reduction in the melting point of sinter mixtures doped with TiO$_2$. However, such low temperature phase assemblies are present at low TiO$_2$ fractions and, as shown by the arrow in Figure 4, increasing the TiO$_2$ 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$_2$ in the sinter mixture).

![Figure 4: A projection of the liquidus surface of the CaO-Fe$_2$O$_3$-TiO$_2$ ternary phase diagram (adopted from Kimura and Muan [6]).](image)

References