Effect of Variation of Alumina on Development of Phases during Iron Ore Sintering

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(Received on July 28, 2008; accepted on October 9, 2008)

1. Introduction

The structure formed during sintering process governs the quality of sinter. Iron ore alumina plays an important role in phases formed, particularly, bonding phase.1–4) Increase in alumina content of sinter adversely affects sinter properties, namely, tumbler strength, reduction degradation index and high temperature properties.5–8) Pimenta et al.1) studied the effect of alumina in the range 1.2–1.7 mass% on sinter structure. The alumina content of sinter was varied by addition of bauxite to the basic sinter mix. They inferred that there was slight increase in ferrite formation at higher additions of alumina. In another study by Pimenta and She-shadri,5) significant diffusion of alumina in hematite crystals was observed during sintering. Indian iron ores contain alumina mostly in the form of iron aluminate (80%) and rest in the form of oxide. Almost all the alumina is segregated in the hematite crystals.

In order to understand the final structure and its evolution for low and high alumina sinters, a comparative study of two Indian ores, one with usual alumina level (H) and another with available low alumina level (L) has been made. Quench pot sintering tests have been used for evolution of phases during different stages in sintering.9)

2. Experimental: Pot Sintering Experiments

A split circular pot (internal diameter 20 cm) of 40 cm height was used in the tests Fig. 1(a). Thermocouples were inserted at three locations T1, T2 and T3 in the pot along the height at a distance of 10 cm, 20 cm and 30 cm respectively from the top. Nitrogen gas was passed from bottom when the middle thermocouple showed maximum temperature. The details of the experimentation has been reported earlier.9) It was possible to stop reactions during different stages of sintering, Fig. 1(b). Samples from the top corresponds very closely to the actual sinter (it has undergone both reduction and oxidation), whereas samples from the middle portion i.e. at the location of the flame front, represents the first melt formed. While the bottom part of the pot had green mix heated and reduced by the incoming gases, Fig. 1(b). All the experiments were repeated twice.

Iron ore 77 mass% (Al₂O₃ ~1.4 mass% and 2.2 mass%, SiO₂ ~1.4 mass%), Lime stone 13.5 mass% (CaO ~51 mass%), Pyroxenite 3.3 mass% (MgO ~55.3 mass%, SiO₂ ~32.7 mass%), Lime ~1.0 mass% (CaO ~85 mass%) and coke breeze 4.5 mass% (ash ~18 mass%) were used in the tests. The details of size of materials used, samples collected and microstructural analysis are same as that reported in Ref. 9).

3. Results and Discussion

3.1. Variation in Alumina

The chemical analysis from different locations of the quenched pot is shown in Table 1. It also shows the standard deviation of FeO. The values are mean of three samples. All the materials melted completely as no free lime was observed.

The melt zone represents the gross melt composition before solidification. When this melt is partially oxidized and solidified, we get the composition of T1. Samples from top resembles very closely to the actual sinter.

Table 1 shows that standard deviation of FeO in all samples except that for melt zone of high alumina ore was about 0.5. But in case of melt zone of high alumina ore, it is high.

Table 1. Chemical analysis of samples from different locations of quenched pot.

| Test No* | Location | Fe, mass % | FeO, mass % | SD of FeO | CaO, mass % | SiO₂, mass % | Al₂O₃, mass % | MgO, mass % | P₂O₅, mass % |
|----------|----------|------------|-------------|-----------|-------------|--------------|--------------|-------------|--------------|
| H        | Top      | 59.3       | 8.4         | 0.3       | 8.2         | 4.2          | 2.2          | 1.6         | 0.18         |
|          | T1       | 58.9       | 7.1         | 0.6       | 8.1         | 4.4          | 2.1          | 1.7         | 0.11         |
|          | T2       | 59.4       | 12.2        | 2.9       | 8.2         | 4.3          | 2.2          | 1.7         | 0.15         |
|          | (Melt zone) |          |             |           |             |              |              |             |              |
| L        | Top      | 59.7       | 9.5         | 0.6       | 8.5         | 4.2          | 1.5          | 1.5         | 0.11         |
|          | T1       | 59.3       | 7.9         | 0.5       | 8.6         | 4.3          | 1.5          | 1.4         | 0.13         |
|          | T2       | 59.6       | 10.5        | 0.6       | 8.3         | 4.3          | 1.6          | 1.5         | 0.12         |
|          | (Melt zone) |          |             |           |             |              |              |             |              |

*H - high alumina ore, L - low alumina ore
much higher, 2.9. The standard deviation of other oxides are 0.5 or lower. This indicates that high alumina melt is significantly inhomogeneous with respect to % FeO compared to that for low alumina melt. The melt FeO also appears to be higher for high alumina sinter than that for low alumina one.

3.2. Maximum Temperature of the Bed

There was no appreciable difference in the maximum bed temperature at two levels of alumina in iron ore. Pimenta et al. observations were otherwise. This may be due to the fact that in our case complete melting was observed in the melt zone itself, whereas in Pimenta’s observation the primary matrix did not melt completely. This was evident by the presence of primary hematite.

3.3. Quantification of Phases and Composition

The phases present along the height for two alumina levels are shown in Table 2 and the composition of phases obtained by optical image analysis is given in Table 3. The composition indicated in Table 3 is an average of ten or more EPMA. Melt zone primarily consists of three types of phases, namely iron oxide, silicate and ferrite/SFCA. It was not possible to distinguish between ferrite and SFCA by optical microscopy. This was resolved by EPMA (Table 3). At melt zone and at T1 location iron oxide was present as a mixture of FeO and Fe₂O₃, and it was not possible to distinguish between these two forms of iron oxides. To distinguish it from hematite and magnetite found on the top, it has been referred as iron oxide in Table 2.

The phases in the melt zone were formed due to solidification of the liquid present in the zone. The solidification of the liquid resulted by partial mixing of melt of the melting zone and its subsequent oxidation gave rise to the phases at T1. The temperature at T1 in case of high and low alumina ores were 667°C and 580°C respectively. These temperatures were obtained when quenching started. Thereby, only solid phase was present at T1. So the phases found at the top was due to oxidation of solid phases and its subsequent transformation.

Table 2 shows that the overall phase percentage at two alumina levels in the melt zone were almost same, but the difference in Al₂O₃ content was reflected in the chemistry of silicate and SFCA phases (Table 3). Secondly, at T1 the amount of phases were different in two cases particularly for silicate. Finally at the top, phase percentage of SFCA, silicate and total iron oxide content (hematite+magnetite) in two cases were similar but their chemistry was different. These observations indicate that the local chemistry of melt formed in the melting zone, the liquid resulted from mixing of the melt and oxidation characteristics were different in two cases.

In the melt zone, iron ore completely assimilated and lime got assimilated as no primary hematite or free lime was observed. Table 3 shows that in case of high alumina ore, silicate formed in the melt zone was 2CaO·SiO₂ type containing very low iron oxide. But in case of low alumina ore, it contained substantial amount of iron oxide and was ternary type. Silicate composition changed very significantly at T1 due to mixing of melt. Compared to silicate formed in melt zone, Fe content is more in case of high alumina ore and less for low Al₂O₃ ore. Figure 2 shows the microstructure of low Al₂O₃ sinter at T1 level. Iron oxide phase is adjacent to silicate phase indicating precipitation of iron oxide from silicate during cooling. This led to lowering of Fe in silicate at T1 compared to that in the melting zone. Further oxidation which led to top sinter, lowers Fe content of silicate in both the cases.

Iron oxide phase formed in the melt zone contained dissolved oxides Al₂O₃, SiO₂, CaO and MgO. Total dissolved oxide in both the cases of low and high Al₂O₃ sinter were similar. Mixing of the melt considerably increased total dissolved oxides in the liquid that solidified as iron oxide at T1. Oxidation of iron oxide phase present at T1 resulted in secondary hematite and magnetite found at the top. During their formation, part of dissolved oxides were rejected and this led to final chemistry of hematite and magnetite. Total dissolved oxides in hematite and magnetite was more for high Al₂O₃ ore.

Transformation characteristic of iron oxide to hematite and magnetite was not identical for low and high Al₂O₃ ore. Table 2 shows that higher alumina samples formed less magnetite compared to low alumina samples. Similar observations was made by Pimenta and Seshadri. There are two important differences in the experiments carried out by Pimenta and Seshadri and present one. Former obtained different alumina level by adding bauxite and ore did not melt completely in their case. But present one is based on ores of two different Al₂O₃ levels and complete melting was

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**Table 2.** Quantification of phases at different levels of alumina by optical image analysis.

| Location | Test No. | Phases | FeO, mass % | Al₂O₃, mass % | SiO₂, mass % | CaO, mass % | MgO, mass % |
|----------|----------|--------|-------------|---------------|--------------|-------------|-------------|
| Melt Zone |           |        |             |               |              |             |             |
| T1       |          | Iron   |             |               |              |             |             |
|          |          | H      | 0.6         | 12.4          | 32.8         | 1.4         |
|          |          | L      | 0.6         | 12.4          | 32.8         | 1.4         |
| T2       |          | Silicate | 1.01       | 10.23         | 34.3         | 1.1         |
|          |          | H      | 0.4         | 1.2           | 3.6          | 1.1         |
|          |          | L      | 0.4         | 1.2           | 3.6          | 1.1         |

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**Table 3.** Composition of phases at different levels of alumina along the height of quenched pot.

| Location | Test No. | Phases | FeO, mass % | Al₂O₃, mass % | SiO₂, mass % | CaO, mass % | MgO, mass % |
|----------|----------|--------|-------------|---------------|--------------|-------------|-------------|
| Melt Zone |           |        |             |               |              |             |             |
| T1       |          | Iron   |             |               |              |             |             |
|          |          | H      | 0.6         | 13.5          | 43.9         | 0.8         |
|          |          | L      | 0.6         | 13.5          | 43.9         | 0.8         |
| T2       |          | Silicate | 0.6        | 1.2           | 2.3          | 0.8         |
|          |          | H      | 0.4         | 0             | 1.5          |             |
|          |          | L      | 0.4         | 0             | 1.5          |             |
| T2       |          | H      | 0.6         | 1.2           | 10.3         | 1.0         |
|          |          | L      | 0.6         | 1.2           | 10.3         | 1.0         |
observed. In spite of this, the observation on the effect of Al$_2$O$_3$ on the relative proportion of hematite and magnetite is similar. This indicate high Al$_2$O$_3$ in sinter always favours higher secondary hematite formation.

In the melt zone, during solidification, melt formed for high Al$_2$O$_3$ ore decomposed to SFCA and Ferrite but due to subsequent mixing and oxidation only SFCA formed at T1. This resulted in increase in amount of SFCA at T1 location compared to that at melt zone as shown in Table 2. There is no significant change in SFCA chemistry from melt zone to top but the chemistry of SFCA for two types ore was different. SFCA formed from low Al$_2$O$_3$ ore had more CaO. The SFCA in both the cases appears to be of M$_{14}$O$_{20}$ type. 

Typical structure from top for two levels of alumina is shown in Fig. 3. The morphology of SFCA formed in the two cases are shown in Fig. 4. It can be seen that in case of high alumina sinter, the SFCA phase is acicular, whereas in case of lower alumina sinter it is dendritic. Difference in chemistry of SFCA phase might be responsible for the structure. The microstructural differences observed in SFCA structure for low and high alumina sinter obtained from the top of the sintering pot was found to be present even in the melting zone. Thereby these structures could be considered as characteristics of the composition of SFCA phase obtained for low and high alumina sinter.

4. Conclusion

(1) The amount of phases in final sinter for ores containing 1.4% and 2.2% alumina were almost same, but the composition and morphology of the phases were markedly different.
(2) Primary melt, in case of high alumina ore, was significantly inhomogeneous compared to that for low alumina melt.
(3) The evolution of phases from melt zone to final sinter is not identical in both cases.
(4) High alumina ore favored higher secondary hematite formation.
(5) Concentration of alumina was observed in hematite and magnetite phases in case of high alumina sinter.
(6) The structure of SFCA in case of high alumina ore is acicular, whereas, in case of low alumina ore, this appears to be dendritic.

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