Study of Liquid Phase Formation during the Sintering of Chromite Pellets and its Effect on the Properties of Pellets

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Abstract

For production of ferrochrome in submerged arc furnace (SAF), chromite ore is used in the form of lumps, briquettes and sintered pellets. The sintered pellets are preferred as a feed in SAF as it improves the furnace performance. During sintering of the green chromite pellets, bentonite reacts with silicate gangues in the chromite and forms the liquid phase which acts as a binder. The physical and metallurgical properties of the sintered pellets depend on the formation of liquid phase. The properties sintered pellets samples collected from the sintering plant were evaluated in the laboratory. The compressive strength of the samples varied significantly from 5 kg/pellet to 305 kg/pellet. The microstructure of the sintered pellets revealed that the porosity and formation of liquid phase affects the compressive strength of the pellets. In addition of this the oxidation of chromite grains during cooling of also influences the strength of the pellets and its metallurgical properties. The results of characterization studies are presented in this research work to relate the liquid phase formation and pellet properties for improved metallurgical applications.

INTRODUCTION

Ferrochromium is produced by carbothermic reduction smelting of chromite in SAF. The electric smelting process for ferrochrome making necessitates the use of a highly permeable lumpy charge for easy dissipation of reaction gases and smooth functioning of furnace. To maximize the utilization of the fines generated in the mining operations agglomeration process is preferred to prepare the suitable feed for furnace operation. Therefore, chrome ore fines and high-grade chromite concentrates are used in the form of pellets and briquettes (Dey et al. 1981). Agglomerates improve the process efficiency in most of metallurgical process. Agglomerates can be loosely defined as an aggregation of particles forming an apparent particle size that is significantly larger than the primary particle size. Such agglomerates can be bound in a variety of ways. Most commonly agglomeration methods used in mineral processing operation are pelletisation-sintering, pot sintering, and briquetting (Watt 1980). The palletising–sintering process developed by Outokumpu is used commonly for production of chromite pellets (Outokumpu 2005). In this process the chromite ore is first ground to -200 mesh size in wet ball mill. The slurry from ball mill is filtered to get the desired moisture. The filter cake is then mixed with binder bentonite and palletised in disc pelletizer. The vertical shaft furnace is used for sintering of green pellets. The pellets are sintered in the temperature range from 1173 K to 1473 K for 6 to 8 hours depending on the process variables. The sintered pellets are then cooled in stream of air. Sintered pellet strength is a function of various parameters such as ore composition, physical properties of ores, ore granulometry, binder characteristics, binder quantity, binder mixing, moisture, coke quantity, coke carbon, sintering temperature and sintering time (Sharma 1992, Nishioka et al. 1996, Akiyama et al. 1991, 1992). Lekatou and Walker (1995) studied the behaviour of chromite pellets and tried to establish relation ship between ore granulometry, pellet size and ore composition.
Mohanty et al. (1981) investigated the heat treatment of Indian chromite ore pellets and reported that strength of pellets increases with increasing sintering temperature in both oxidized as well as reduced pellets but oxidised pellets shows higher strength than reduced pellets due to slag forming bonds.

**EXPERIMENTAL WORK**

The filter cake, green pellets and sintered pellets samples were collected from Pelletization and Sintering plant for physical and chemical characterisation. Chemical analysis of sintered pellet was carried out using conventional wet chemical techniques. Compressive strength of the pellets was measured using universal testing machine. The sintered samples were divided into 3 categories based on their compressive strength, (a) less than 60 kg/pellet, (b) between 60 and 150 kg/pellet and (c) more than 150 kg/pellet. The sintered pellets samples were cut into half and used for preparation of samples for microscopic examination. A vacuum impregnation method was used for mounting the samples in resin. The samples for microscopic examination were prepared by grinding with emery paper followed by polishing with diamond paste. Polished samples were examined first under Axiosplan2 universal metallurgical microscope attached with AxioCam HRc digital camera and AxioVision 4 image analysis software. The phase composition was carried out using a scanning electron microscope (JEOL JXA-6400 series), which was operated at 15 kV accelerating voltage. The semi quantitative analysis of various phases was carried out using, KEVEX superdry, EDX detector.

**RESULTS AND DISCUSSION**

The chemical composition of sintered pellettes of various strength is given in Table 1, which clearly shows the influence of charge composition on the strength of the pellettes. The results of chemical analysis demonstrate that the strength of pellet mainly depends on SiO₂ content and Cr:Fe ratio of chromite feed. Higher strength pellets have low Cr:Fe ratio and higher silica concentration. Whereas pellets with high Cr:Fe ratio and low silica content have lower strength. The optical photomicrographs of the sintered pellets are shown in Figures 1a to c. Figure 1 shows the variation in the porosity of the sample and amount of liquid phase formed during sintering process (marked with circle). The back scattered electron (BSE) microstructures of the samples are shown in Figures 2 to 4. The bright phases in the microstructure are the Fe-rich oxide phases formed due to oxidation during air cooling after sintering. The amount of bright phase i.e. oxidation product also varies in pellets of different strength. In Figure 2 the microstructure of -60 kg strength pellets shows the loose / weak bonding of the chromite grains. It also shows the small fraction of oxidised bright phases and formation of cracks in the chromite grains. Whereas in Figure 3, moderate oxidation and formation of bonds with micro-porosity along the chromite—liquid phase interface was observed in microstructure of medium strength pellets (60 – 150 kg). Strong bonding of chromite particles with large oxidised regions was observed in the microstructure of high strength pellets (>150 kg strength) in Figure 4. The microscopic examination of sintered pellets revealed that in addition to porosity, the formation of liquid phase during sintering and subsequent oxidation of chromite grain during cooling also influence the strength of sintered pellets.

<table>
<thead>
<tr>
<th>Strength (Kg/pellets)</th>
<th>Fe(T)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
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</thead>
<tbody>
<tr>
<td>0 to 60</td>
<td>12.55</td>
<td>2.44</td>
<td>5.96</td>
<td>13.65</td>
<td>12.57</td>
<td>46.47</td>
</tr>
<tr>
<td>60 to 150</td>
<td>13.38</td>
<td>2.42</td>
<td>5.85</td>
<td>13.75</td>
<td>12.74</td>
<td>45.29</td>
</tr>
<tr>
<td>&gt;150</td>
<td>12.90</td>
<td>2.41</td>
<td>7.79</td>
<td>13.55</td>
<td>12.15</td>
<td>44.55</td>
</tr>
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</table>
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Fig. 1: Optical Photomicrographs of the Sintered Pellettes of Different Compressive Strength. the Bright and Grey Colour Phases are Chromite Particles Whereas Dark Grey Colour Phases Marked with Circle are Silicate (Liquid) Bonding Phase

Fig. 2: Back Scattered Electron Image of Sintered Pellets of - 60 Kg Strength
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Formation of Liquid Phase
Sodium bentonite (Na,Ca)0.3(Al,Mg)2Si4O10(OH)2 \cdot n(H_2O) has strong swelling properties and possesses a high dry-bonding strength. Therefore it is used as a binder in pellettization process. The bentonite gives required strength to the green pellets. During sintering, bentonite and other silicate gangue in the chromite react at high temperature with each other and form low temperature liquid phase (alkali silicates). The physical and chemical properties of this liquid phase depend on its composition (SiO_2, Al_2O_3, CaO, Na_2O) and firing temperatures. The microstructure and EDX analysis of phases present in sintered pellet of 60-150 kg strength are presented in Figure 5. The higher firing temperatures, high level of bentonite and silicate gangue in the charge enhance the solubility of other silicates in the liquid phase and thereby increase the volume/amount of the liquid phase. At high temperature viscosity of liquid phase reduces which helps the liquid phase to fill the voids between the chromite particles resulting in pellets with low porosity and high compressive strength. Figure 5 also confirm the effect of silica on strength of pellets. Reactivity of very high strength pellets in smelting process is lower due to poor porosity and also formation of silicate layer on the surface of chromite grains which retard the reaction of chromite with reductants (CO, C, Fe_3C etc.). In the early stages of reduction-smelting process in the SAF, silicate phase in the sintered pellets adheres to the surface of electrodes and other furnace parts in the top and middle regions and results in the formation of crust. These processes degrade the furnace performance.

Oxidation of Chromite Grain During Cooling
Forced air cooling technique is used in vertical shaft furnace to cool the sintered pellets. During cooling the air also oxidises the FeO in the chromite spinels and partially reduced Fe-sesquioxide during sintering. FeO from chromite spinel oxidises and forms the Fe_2O_3-Fe_3O_4 precipitates on the chromite grains (bright grey phase 1 in Figure 6) depending on the oxygen partial pressure (P_{O_2}) inside the furnace cooling zone. Improper conditions during reduction and subsequent oxidation of Fe^{2+} in chromite grains results into formation of micro-cracks. The ionic radius of Fe^{2+} is larger than the space available at the tetrahedral site in chromite spinel lattice this causes the dilation of lattice in \{111\} direction (Tathavadkar et al. 2005). The lattice strain generated due to dilation results in the micro-cracking of chromite phase. The micro cracks reduce the strength of the pellets.

CONCLUSIONS
In the detailed microstructural studies of sintered chromite pellets it was found that liquid phase play a crucial role in strengthening of chrome ore pellets. Liquid phase also control the porosity as well as distribution of pores inside the pellet which control the metallurgical behaviour of pellets in the
submerged arc furnace in the ferrochrome making process. It was also found that in low strength pellets the liquid phase formation is found in nascent stage whereas it is dominant in high strength pellets and hence increases the pellet strength. Bentonite, a binder, plays a vital role in formation of low melting point silicate liquids which cover up the chromite particles in bonding process. Silicate and iron oxide concentration in the charge play a significant role in pellet strengthening and improper oxidation of Fe cause lattice deformation and formation of microcracks which in turn reduces the pellet strength.

![Fig. 5: Microstructure and Edx Analysis of Binder Phase and Chromite Grains in the Sintered Pellettes of 60-150 Kg Strength](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cr$_2$O$_3$</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
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<tr>
<td>1</td>
<td>50.83</td>
<td>0.42</td>
<td>13.54</td>
<td>29.54</td>
<td>0.54</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>47.87</td>
<td>19.93</td>
<td>14.90</td>
<td>11.36</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>0.83</td>
<td>0.90</td>
<td>8.22</td>
<td>0.64</td>
<td>77.64</td>
<td>2.97</td>
<td>2.80</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>0.82</td>
<td>0.65</td>
<td>6.48</td>
<td>0.57</td>
<td>80.61</td>
<td>2.45</td>
<td>1.91</td>
<td>0.68</td>
</tr>
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</table>

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**REFERENCES**