REFINING OF FERRO-SILICON

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1. Introduction

The ferro-silicon required for making electrical steels must have low content of aluminium, calcium and carbon. But the ferro-silicon produced by carbothermic reduction process contains appreciable quantities of these impurities particularly aluminium, calcium and oxygen. Hence efforts are being made to develop economically viable techniques for the refinement of commercial grade ferro-silicon for use in the making of silicon steels. The increased interest in the refining of ferro-silicon is mainly due to its growing demand in the production of Cold Rolled Grain Oriented (CRGO) high permeability electrical steels [1].

There are four principal grades of ferro-silicon which are manufactured by carbothermic process in the electric arc furnace and they contain approximately 15, 50, 75 and 90 percent of silicon. Typical analysis of these grades are given in Table 1. The most objectionable impurities in these ferro-silicon are the oxides of aluminium, calcium and titanium. Their presence brings down the magnetic permeability and increases the core loss, that is the watt loss which is comprised of hysteresis loss and eddy current loss in silicon steels. The magnetic flux and the total magnetic properties get reduced thereby minimising the electrical properties.

This paper focusses on various methods of making low aluminium ferro-silicon from the commercial FeSi-75. Literature review on the refining of ferro-silicon shows that there are two principal grades of refined Fe-Si-75. Table 2 shows the specifications of these grades. On comparison with Table 1, it is clear that refining in respect of all impurities is essential to make it useful for the production of silicon steel [2,3].

2. PROCESSES FOR THE REFINING OF FERRO-SILICON

The following methods are considered to achieve low aluminium in FeSi-75:

1. Solid/liquid oxide methods
2. Oxidising treatment with gaseous/enriched air
3. Refining with chlorine gas
4. Purification by carbon dioxide gas

2.1 Solid/Liquid Oxide Method

Kravchenko and Serebrennikov reported the large scale trial of the refining of industrial ferro-silicon 75 in an electric arc furnace using synthetic silicate slag of CaO-SiO₂ [4]. This method reduced aluminium content from 1.5 percent to below 0.1 percent, calcium level from 1.3 percent to 0.08 percent and carbon content from 0.09 percent to 0.05 percent. In this case experimental trials were conducted in an acid electric steel melting furnace at Zaporzhe Ferro
Alloy Works, Russia. The basicity defined as:

$$B = \frac{(CaO+MgO)}{SiO_2}$$

was kept constant around 0.6 and the operating temperature was 1600°C. The relationship of aluminium content of the refined ferro-silicon was reported to be as follows:

$$C_{Al} = 0.08 + 12(B-0.6)^2$$

(1)

where, $C_{Al}$ is the concentration in the refined ferro-silicon. The tap to tap time has been related to refined ferro-silicon as follows:

$$C_{Al} = 0.1 + \frac{1.49}{1+22(\tau-1.25)^2}$$

(2)

where $\tau$ lies between 1.25 to 2.5 hour with the slag basicities between 0.4 to 0.7 for the 500 kg charge. The silicon loss has been reported to be 7.4 percent due to the sublimation of the toxic vapour like silicon monoxide (SiO).

The mechanism by which ferro-silicon is refined can be represented as follows:

$$SiO_2(s) + CaO(s) = CaO.SiO_2$$

(3)

$$SiO_2(s) = (SiO_2)$$

(4)

$$2[Ca] + (SiO_2) = 2CaO + [Si]$$

(5)

$$2[Al] + 2(SiO_2) = (Al_2O_3) + [Si] + SiO(g)$$

(6)

$$SiC(s) + (SiO_2) = [Si] + SiO(g) + CO(g)$$

(7)

$$CaO.SiO_2(1) + (Al_2O_3) + (SiO_2) = (CaO.Al_2O_3.2SiO_2)$$

(8)

where the letters s, l and g relate to the solid, liquid and gaseous substances respectively and the square bracket and round brackets denote the compounds dissolved in the metal and the slag phases, respectively.

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The power consumption was reported to be of the order of 1400-1500 kWh/ton. The carbon in the ferro-silicon is present as silicon carbide.

A different approach was to improve upon the process and the quality of electrical steel. In this approach at Kuznetsk Ferro Alloy Works, Russia, trials were conducted in the industrial conditions for removing aluminium from high levels in the ferro-silicon melts down to a level of 0.1 percent or less. The approach consists of treating the melt outside the furnace with an oxidising slag consisting of sederite (45% FeCO_3), fluorospar (CaF_2) and injecting under the melt a gas mixture containing 81-82 percent oxygen and 18-19 percent nitrogen (by volume). The average silicon burn up in the process was approximately 9-10 percent.

2.2 Oxidising Treatment with Gaseous Oxygen/Enriched Air

McClellan patented a process in 1967 for refining of ferro-silicon 75 by the direct oxygen injection technique [5]. The process comprises of a molten bath of metal to be purified and treating the surface of the molten metal with a stream of gaseous oxygen. An inert gas was simultaneously introduced from the bottom of the molten bath to provide agitation. This helped
in the oxidation process of impurities effectively. The process was carried out at a temperature of 1350°C to 1700°C. The results suggested that oxygen flow should be about 1 to 2 times the rate of flow of argon. The limitations of the process are that the impurities, such as, aluminium and calcium in 74 to 76 percent ferro alloy should not be more than 0.45 percent and 0.20 percent respectively. Because of the patented nature of the process the information is not available in detail. However the patent claimed that there is no substantial silicon loss.

2.3 Refining with Chlorine Gas

Wise reported in 1960 the refining of ferro-silicon by injecting chlorine deep inside the ladle of molten bath [6]. Chlorine injection was carried out by hydraulically operated dispenser tubes. The author reported that chlorine requirement was of the order of 30 parts per 1000 parts by weight of the melt. During the process the silicon level got reduced because of volatilisation to silicon tetrachloride and calcium chloride level thus formed cannot be removed completely. Silicon level had to be replenished for adhering to the required composition. Further removal of aluminium level to less than 0.1 percent was not possible.

2.4 Purification by Carbon Dioxide Injection Method

In contrast to the chlorination process for the refining of ferro-silicon which suffers from serious shortcomings as being the environment aggressive process, the carbon dioxide injection method is somewhat safer being an environment friendly technology. Strauss [7] and Tuset [8] separately claimed the process to be convenient and simple. In this method carbon dioxide gas or a combination of carbon dioxide and oxygen gas is injected along with the addition of lime as a slag forming flux. The oxides of free aluminium, calcium and silicon make a slag forming component having composition CaO.Al₂O₃.2SiO₂ which floats on the top of the melt. It is separated during the tapping of the refined material. The patent further claims that the effective control of the process can be achieved during the processing with carbon dioxide gas injection.

In a typical example, the refining of FeSi-50 containing 47 percent silicon and 50 percent iron, 1.32 percent aluminium and 0.15 percent calcium, 57 lbs of carbon dioxide gas at an average feed rate of 1.21 lbs of carbon dioxide per minute is required. This brings down the aluminium content to 0.22 percent and calcium to 0.02 percent. Thus 83.3 percent of aluminium and 87 per cent of calcium were removed. An important advantage of the process is that the waste products of the reaction do not remain as contaminants unlike chlorination process and the reaction is exothermic. The use of pressurised carbon dioxide cylinders resulted in considerable chilling effect thereby causing skulling. The reaction time is around 47 to 48 minutes.

3.0 TYPICAL RESULTS FROM STUDIES ON THE REFINING OF FERROSILICON CARRIED OUT AT NML

3.1 The Chlorine Donor Method

One kg melt of FeSi 75 was refined in a graphite crucible fitted in an induction furnace by the addition of 400 gms of hexachloroethane tablets at 1450°C. The melt was treated for
30-35 minutes. The impurity, aluminium was removed as aluminium chloride. As a result of refining the aluminium level in FeSi-75 was reduced from 1.4% to 0.23%. The silicon loss was about 7-11 percent.

3.2 The Carbon Dioxide Injection Method

One kg melt of FeSi-75 was refined in an induction furnace by the addition of 30-35 gms of lime power followed by the injection of 90-120 liters of carbon dioxide/hour for about 45 minutes at 1500-1550°C. The aluminium of the melt was oxidized to aluminium oxide, calcium to calcium oxide and a small part of silicon to silicon dioxide. The slag of the composition CaO Al₂O₃·2SiO₂ floated at the top of the melt. The slag was removed and refined metal was separated. As a result of refining, the aluminium level in FeSi-75 was brought down from 1.4% to 0.19%. Graphite dispenser tube was used for the injection of Carbon dioxide gas and silicon loss was 2 to 3%.

3.3 The Oxygen Injection Method

One kg melt of FeSi-75 was refined in an induction furnace by the addition of 20-25 gms of lime powder followed by the injection of oxygen at the rate of 80-90 litres per hour for about 40 minutes at 1450-1500°C. The slag of composition CaO Al₂O₃·2SiO₂ was formed and floated at the top of the melt. The slag was removed and refined metal was separated. Here the aluminium level in FeSi-75 was brought down from 1.4% to 0.20%. Graphite dispenser tube was used for the injection of oxygen gas and silicon loss was about 3 to 5%.

4. CONCLUSIONS

Out of the several processes of ferro-silicon refining, discussed above oxygen injection method, carbon dioxide injection method and synthetic slag method are relatively attractive as they effectively bring down the aluminium level and are free from polluting gases. The carbon pick up is usually higher in a graphite crucible; therefore mullite reactor and mullite dispenser tubes are suggested for the refining of ferro silicon in large scale trials. Large scale trials for refining FeSi-75 in an industrial induction furnace are needed to prove the viability of NML technology.

References

1. Datar N S; Proceedings of national seminar on elect. steels, Jan.18, RDCIS, Ranchi 1983
4. Kravchenko V A and Serebrennikov; Steel (English), December, pg 1003-1005, 1967
## TABLE 1
### TYPICAL ANALYSIS OF FERRO-SILICON

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition of grades, % (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Silicon</td>
<td>14-17</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Calcium</td>
<td>Trace</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.03-0.05</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.03-0.09</td>
</tr>
<tr>
<td>Iron</td>
<td>Balance</td>
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</table>

## TABLE 2
### SPECIFICATION OF REFINED FERRO-SILICON 75

<table>
<thead>
<tr>
<th>Component</th>
<th>Standard Grade (wt/wt)</th>
<th>High Purity Grade (wt/wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>76.00</td>
<td>76.00</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.18</td>
<td>0.08</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Other residual</td>
<td>0.75</td>
<td>0.40</td>
</tr>
<tr>
<td>Iron</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
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