Refining of High-carbon Ferromanganese

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Abstract

Due to high affinity of metals towards carbon, the reduction of manganese ore by carbon results in high-carbon ferroalloy. This carbon being a deleterious impurity whether the metal is used as ferroalloy or an austenite stabilizer for stainless steel, use of low-carbon ferromanganese is indispensable. The conventional methods of carbon removal are multi-stage, cumbersome and involve loss of metal in slag. Attempts have been made in the present investigation to explore non-conventional methods such as solid-state decarburization. This reduces loss of metal as there is no slag formation and the carbon removal is carried out by gaseous oxidizer like carbon dioxide which is provided externally or generated in situ. The preliminary findings show that the mechanism of decarburization is quite complex, as solid-gas reactions viz. oxidation of manganese and carbon take place simultaneously. It has been shown that maximum decarburization with minimal loss of metal can be achieved simultaneously by choosing appropriate experimental conditions. From the experimental evidence of the present investigation, it can be concluded that solid-state decarburization of high-carbon ferromanganese consists of multtiple steps in which carbon rich carbides gradually transform into metal rich carbide. Based upon the observations, it can be inferred that, the efficiency of this particular technique can be improved by increasing the operating temperature, decreasing the particle size of the reactants and lowering the partial pressure of effluent gas viz. CO without vaporization losses of metallic manganese.

Key Words : decarburization, manganese, carbides, kinetics

Introduction

When ferromanganese is produced by reduction of MnO using carbon as a reductant in submerged arc furnace, the product so formed is basically carbon saturated iron-manganese alloy. Since manganese has a strong affinity towards carbon, formation of manganese carbides can not be prevented. In spite of this disadvantage, this process is still being popularly used as it can produce high-carbon ferromanganese economically [1].

The higher percentage of carbon in ferromanganese is undesirable and subsequently creates further problems *viz.* sensitization [2], provokes brittle fracture at cryogenic temperatures. To overcome the aforesaid lacunae, although various researchers made attempts for removal of carbon, but most of the techniques were associated with drawbacks such as involvement of multiple stage processes, high refractory consumption, high energy consumption and poor metal recovery due to losses of metal in slag, fumes [3].

The non-conventional method uses various oxidizers *viz.* steam [4], iron oxide, silica [5], oxygen [6] for selective oxidation of carbon. Research is also in progress on current techniques *viz.* D.C. arc furnace [7] and thermal plasma route [8-10] for high-carbon ferromanganese production.

Attempts to remove carbon by the methods used in steel making cannot be applied to ferromanganese because the loss of manganese in slag cannot be prevented. In fact, it is likely to be more due to very high vapor pressure of manganese. During oxygen lancing the temperature produced is sufficiently large enough to cause appreciable losses of manganese in the form of fumes.Considering these two reasons it would be uneconomical to carry out the decarburization in liquid state.

In this project, therefore an attempt has been made to find a simple technique for decarburization. It is aimed to study the feasibility of solid-state decarburization of high-carbon ferromanganese by non-conventional gaseous as well as solid oxidizing agents *viz.* carbon dioxide and manganese carbonate and/or manganese dioxide respectively. The idea is to obtain a semi-refined product which can be blended with low-carbon ferromanganese available in the market so as to produce major quantum of extra low carbon steels economically.

Experimentation

The experimental setup consisted of fabrication of the Kanthal wound resistance heating furnace capable of reaching 1473 K. The main reaction chamber consisted of an impervious, recrystallized alumina tube. It's both open ends were sealed with indigenously fabricated couplings of stainless steel of AISI grade 316. They had provision for gas inlet and outlet ports. The chamber could be evacuated up to 10^{-6} torr by operating combination of rotary and diffusion pump. Vacuum level was monitored with combined digital pirani-penning gauge. Desired temperature was achieved by feeding power to the furnace through an auto-transformer, solid-state relay and temperature controller cum indicator. The temperature sensor was a calibrated K type chromel - alumel thermocouple [11].

High-carbon ferromanganese lumps were pulverized in a zirconia ball mill for about six hours. The product was subjected to sieve analysis. Particle size measurement was done for the selected sets of powder for investigation. Chemical analysis of the sample indicated 75, 15, 6.88 and 2 weight per cent of Mn, Fe, C and Si respectively [12-14]. The material characterization of high-carbon ferromanganese involved X-ray diffraction analysis using an iron target [15-17]. A known mass of mixture of high-carbon ferromanganese and MnO_2 or $MnCO_3$ in the stocihiometric ratio was taken in the form of pellet having aspect ratio unity (height = diameter = 1 cm). The pellet was placed in a recrystallized alumina boat of known mass. The remaining procedure was identical as aforementioned except in lieu of carbon dioxide atmosphere [11] samples were subjected to pyro-vacuum treatment. Similar sets of experiment were carried for various particle sizes of high-carbon ferromanganese, duration temperature and pressure.

Results & Discussions

Results indicated in the Figure 1 reveals that, the extent of decarburization was found to increase with rise in temperature. However, $MnCO_3$ seems to be comparatively better decarburizer than $CaCO_3$ [18]. This is attributed to its comparatively low endothermic decomposition temperature. Also the additional advantage with it is unlike $CaCO_3$, it does not produce heterogeneous material *viz.* CaO which not only impedes mass transport of the product gas but has to be removed at subsequent stages by leaching the product with dilute hydrochloric acid. On the other hand with $MnCO_3$ as an oxidizer, the total metal content in the charge is increased. Furthermore, the MnO that is formed could react with carbon especially at low pressures to enhance the decarburization [19-20].

Kinetics of the Process

In later stage of the investigation, $MnCO_3$ was substituted with MnO_2 and further studies were carried out on decarburization kinetics. In this case, overall rate of decarburization is governed by many variables. However, due to certain practical limitations the spectrum of the process variables to be investigated was restricted to the decarburization period, temperature, particle size of the reactants and reduction of ambient pressure.

Effect of Time

From the graphical illustration of the experimental data as described in the Figures 2 to 4, in general it was observed that the maximum decarburization was obtained over the span of 2.5 to 4.5 hours with tolerance of ±0.5 hour, for a fixed set of parameters such as temperature, pressure and particle size. The decarburization period was restricted to 6 hours because beyond this time further decarburization was found insignificant.

Effect of Temperature

The temperature of decarburization should preferably be maintained around 1373 K so as to compensate the heat losses due to endothermic reaction imparting thereby more driving potential for completion of decarburization reactions leading to about 60 per cent carbon removal as illustrated in the Figure 2.

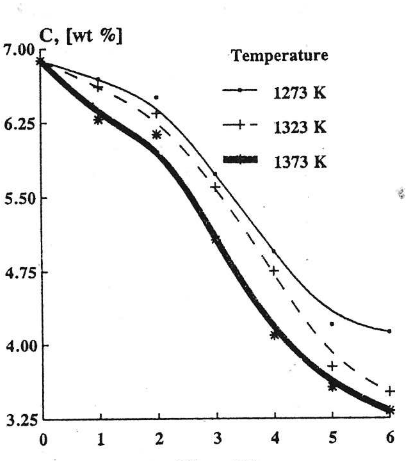

Figure 1 : Decarburization of 49 µm high-carbon ferromangnaese by $MnCO_3$

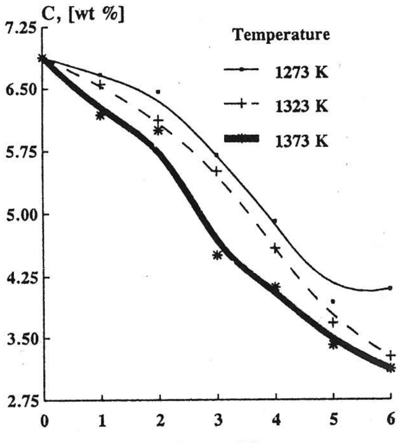

Figure 2 : Effect of temperature on decarburization of 49.5 µm HC Fe-Mn

Effect of Particle Size

The Figure 3 shows that, the high-carbon ferromanganese of particle size in the range 45 to 53 μm was found comparatively more effective than 90 to 105 μm. This is due to the availability of large number of reaction sites due to the decrease in grain size which consequently increases the reaction velocity [21-22].

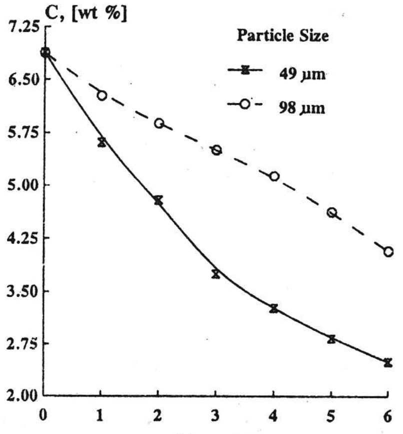

Figure 3 : Effect of particle size on decarburization at 1373 K, 0.001 Torr

Effect of Pressure

As shown in the Figure 4, lowering of the partial pressure of the product gas by application of vacuum considerably improved the efficiency of the decarburization process. Manganese enrichment of the order of 82 weight per cent simultaneously with good extent of decarburization was obtained by subjecting the reacting mass to vacuum of the order of 0.001 torr.

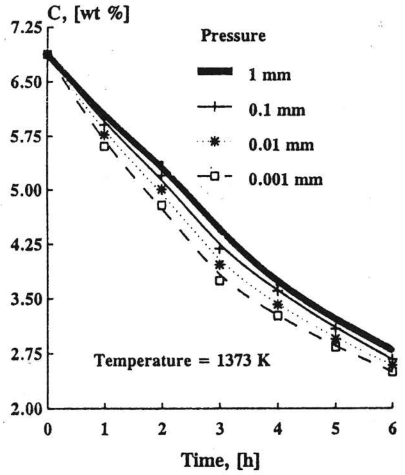

Figure 4 : Effect of vacuum on decarburization of 49.5 μm HC Fe-Mn

Effect of Nature of the Oxidizer

The effect of the nature of the oxidizer on the extent of decarburization was studied by making thin sections of the decarburized ferromanganese with the aid of a diamond wheel. They were subjected for carbon and manganese analysis. The data for the elemental concentration profiles for manganese and carbon thus obtained are as shown in the Figures 5 and 6. The decarburization by external gaseous oxidizer *i.e.* CO_2 technique seems to be limited with the peripheral boundaries as shown in the Figure 5. On the contrary, as evident from the Figure 6, in an *in situ* solid oxidizer *i.e.* MnO_2 method the extent of decarburization was more and uniform.

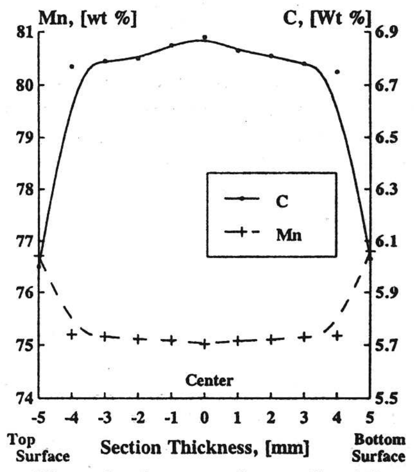

Figure 5 : Concentration profile of C & Mn for gaseous oxidizer technique

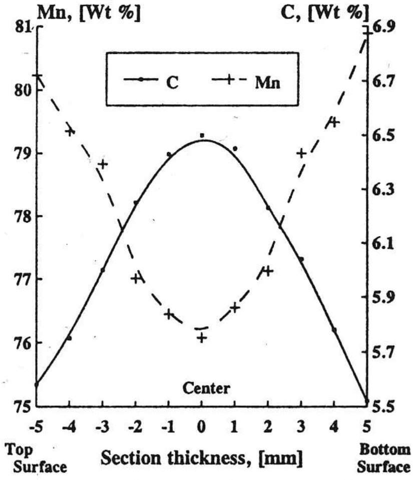

Figure 6 : Concentration profile of C and Mn for solid oxidizer technique

Conclusions

From the experimental evidence of the present investigation, it can be concluded that the solid-state decarburization of high-carbon ferromanganese consists of multiple steps in which carbon rich carbides gradually transform into metal rich carbide.

Overall, the salient features of the solid-state, decarburization technique are its simplicity of operation without slag formation thereby preventing corrosion of refractory of the furnace and metal losses in slag. Besides these, it can be inferred that, the efficiency of this particular technique can be improved by increasing the operating temperature, decreasing the particle size of the reactants and lowering the partial pressure of the effluent gas like CO without vaporization losses of metallic manganese.

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