

Solid-state Decarburization of High-carbon Ferromanganese

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Because of its unfavourable manganese-to-carbon ratio, high-carbon ferromanganese is unsuitable as an alloying agent for the production of alloy steels like Hadfield steel. This is true in other applications as well, viz coating on welding electrodes, where a high proportion of carbon is undesirable. The problems arising due to excess carbon are overcome by decarburization of the parent source, i.e. high-carbon ferromanganese, by conventional and non-conventional techniques. In the conventional method, silicon acts as a reducer. Hence, the production of low- or medium-carbon ferromanganese involves two steps: (1) the production of silicomanganese with 15 to 20 per cent silicon, and (2) the reaction of silicomanganese with MnO-rich slag. The non-conventional method makes use of various oxidizers such as steam, silica, and iron oxide for selective oxidation of the carbon. The use of oxygen in top- and bottom-blown MOR was also attempted.

In view of the disadvantages associated with these techniques, viz high refractory consumption, loss of manganese in slag and fumes, the present investigation attempted to find a simple method for solid-state decarburization by carbon dioxide or calcium carbonate. During decarburization, Mn_3O_4 and MnO, which are formed as intermediate products, are allowed to react further with manganese carbides in an inert atmosphere. This helps to produce a refined product, which, when mixed with the low-carbon ferromanganese available in the market, will give a blend that can be used for the economic production of manganese steels and alloys.

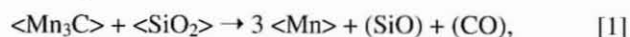
In an investigation of the kinetics of the process, the effect of temperature on decarburization was studied.

Introduction

Ferroalloys are manufactured by electrothermal processes with carbon as a reductant and electrical energy as a source of heat. Owing to its high affinity for carbon, the smelted ferroalloy invariably contains substantially large amounts of this undesirable element, ranging from 6 to 8 weight per cent. The presence of carbon is a crucial factor when ferroalloys are added in the production of alloy and special steels. In certain cases, carbon is the main cause of problems, e.g. sensitization in stainless steels. Attempts to reduce the carbon content in a manner similar to that employed in steelmaking invariably result in oxidation of the metal to a greater extent, ultimately affecting the recovery of the metal and increasing the cost owing to the loss of metal in the slag. The production of low-carbon ferroalloys is therefore a multistage process needing precise control at every stage.

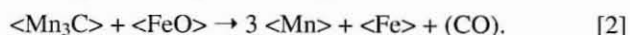
Low-carbon ferromanganese in the form of lumps and powder finds wide applications in the ferrous and non-ferrous industries, e.g. as coatings for welding electrodes. This low-carbon ferromanganese is produced via an intermediate product, silicomanganese, and its refining by lime, with considerable loss of manganese as MnO in the slag. This fact reveals how uneconomical the conventional technique is.

This particular situation has encouraged researchers to find an alternative technique for the decarburization of high-carbon ferromanganese. In the USA¹ attempts were made to refine ferromanganese by silica under vacuum, according to the reaction

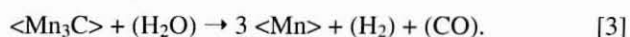


where $<>$ = solid, and $()$ = gas phase.

The product was, however, contaminated with unreduced silica. Moreover, owing to the production of carcinogenic gaseous SiO, it was difficult to maintain the vacuum. Also, the reaction was kinetically unfavourable. Even FeO has been tried for the refining of high-carbon ferromanganese under vacuum. Here the product obtained is low in carbon, but of a lower grade owing to its incorporation of reduced iron:



Decarburization of high-carbon ferromanganese with steam² has also been attempted, but this is a slow and endothermic process:



The production of low-carbon ferromanganese by the Thermit³ technique is associated with an extremely violent reaction, which can even lead to explosions:



$$\Delta G^\circ = -1739,75 - 0,083 T \text{ kJ}.$$

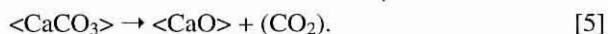
Moreover, the product contains appreciable amounts of reducing agent, viz aluminium.

Similar problems arise with silicon as a reducing agent.

The presence of these elements may be objectionable for some applications. Ferromanganese production by solid-state reduction and carburization of the metal values contained in low-grade ore, waste slag, and purified oxides can be a promising alternative to conventional smelting techniques⁴. According to Kotava⁵, molten high-carbon ferromanganese can be decarburized in two stages, i.e. top-blown oxygen plus bottom-blown argon in the first stage, followed by the gradual blowing of oxygen–argon mixture in the ratio 2 to 0,3 to yield a product containing 75 per cent manganese and 0,87 per cent carbon. Dresler^{6,7} has reported manganese recoveries of 80 to 90 per cent, the exact recovery being a function of the slag volume. Lee⁸ has studied the thermodynamics of smelting and refining of high-carbon ferromanganese, which give a reasonably good description of the high-carbon ferromanganese operation.

A lot of work is also in progress on the MOR⁹, thermal plasma¹⁰, and d.c. arc-furnace¹¹ routes for the production of low-carbon ferromanganese. In all these processes, there is always a certain degree of loss of metal in the slag. The present work aims at carrying out the removal of carbon without appreciable loss of metal. This is possible by bringing about the decarburization reaction in the solid state with a gaseous reactant such as carbon dioxide. Carbon dioxide was chosen for the following reasons.

- Solid–gas reaction is always more favourable kinetically than solid–solid reaction.
- At the experimental temperatures, the carbon monoxide that is formed, owing to its high diffusivity, is easily removed from the reaction site.
- The gaseous reactant can be generated by the thermal decomposition of solid carbonate, e.g. calcium carbonate, which can be mixed with the solid reactant, i.e. high-carbon ferromanganese. Hence, in this work studies were also carried out on the decomposition of carbonate:



Experimentation

For favourable kinetics of the solid–gas reaction, the experiments were carried out using fine high-carbon ferromanganese powder (53 μm) with close tolerance of mesh size. The carbide present in high-carbon ferromanganese was predominantly Mn_3C as detected by material-characterization studies involving X-ray-diffraction (XRD) analysis using a Philips PW-1820 diffractometer with an iron target. The initial assay of the sample showed it to contain 6,88 weight per cent carbon, 75 per cent manganese, 15 per cent iron, and 2 per cent silicon. Two sets of experiments were carried out.

External Gaseous Reactant

In the initial stages, the reacting gas (carbon dioxide) was generated at ambient pressure by the use of Kipps' apparatus. The moisture was removed by passing the gas through molecular sieves and a P_2O_5 trap. However, the results of

the decarburization, even at high temperature, were not encouraging and, hence, in the subsequent stages high-purity carbon dioxide along with the carrier gas, argon (IOLAR–III), was used. The comparable molecular weight of these two gases ensured uniform composition of the gas mixture.

A sample of high-carbon ferromanganese powder of known mass (5 g) was placed in a recrystallized-alumina boat of known mass. The sample was loaded into the reaction tube, and the furnace was set to 1273 K. The temperature was achieved by precise control of the power input to the Kanthal-wound 2,5 kW furnace through an autotransformer, solid-state relay, and digital temperature-controller indicator. The temperature was measured by use of a calibrated 26 s.w.g. chromel–alumel thermocouple¹². The sample was exposed to a stream of carbon dioxide current (flowrate 20 ml/min) at 1273 K for a fixed time (4 h), and was then furnace-cooled to room temperature. The change in mass of the sample was carefully recorded, and it was pulverized for chemical analysis and XRD studies. Similar experiments were carried out at different temperatures and for different durations.

In Situ Gaseous Reactant

In this set of experiments, high-carbon ferromanganese powder was mixed in stoichiometric proportion with A.R.-grade precipitated calcium carbonate, i.e. 1,4:1 by mass. The two components were mixed thoroughly, and a known mass of the sample was subjected to decarburization by the same procedure as described above. At the end of each experiment, the product was leached with 1 per cent hydrochloric acid until it gave a constant mass, assuring complete removal of CaO without affecting the metal content. The sample was dried thoroughly, weighed, and subjected to chemical and XRD study.

Results and Discussion

In view of the lack of earlier work reported by this method, the main emphasis in the present investigation was on the feasibility of the process. Hence, no attempts were made to achieve very low levels of carbon (<0,01 per cent), and the efficiency of the process was measured in terms of percentage carbon removal and manganese enrichment. Accordingly, the studies were confined to some of the variables that would affect the kinetics of the process.

The loss in mass from each carbide is due to the gasification of carbon to carbon monoxide by carbon dioxide:



Thermal decomposition of calcium carbonate also causes a loss in mass of the specimen. Further, there is mass gain due to the formation of MnO and Mn_3O_4 . Because of such complexities, the progress of the reaction could not be monitored by the measurement of mass losses. Instead, the test samples were removed successively at regular intervals and were analysed independently for carbon and manganese according to Young's¹³ method.

The results thus obtained are shown in Figures 1 to 9. Figures 3 and 4 show that carbon dioxide at slightly excess pressure is comparatively more effective than that at ambient pressure (Figures 1 and 2). In the initial stages of the external oxidizer technique, externally generated carbon

dioxide at high temperature was more effective. With flowing gas at high pressure, the decarburization was efficient in the initial stages, but later the rate decreased, probably owing to sintering of the solids, which reduced the porosity and hence the contact between the reactants.

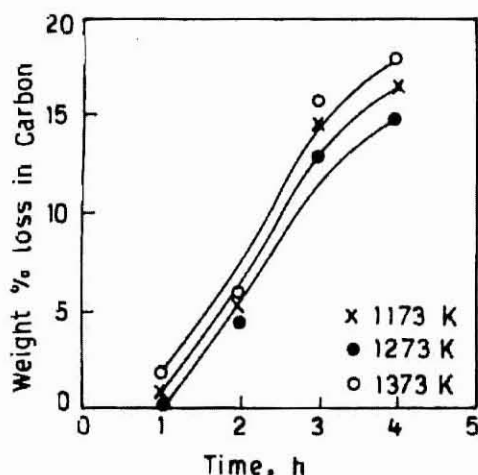


FIGURE 1. Decarburization by carbon dioxide at ambient pressure

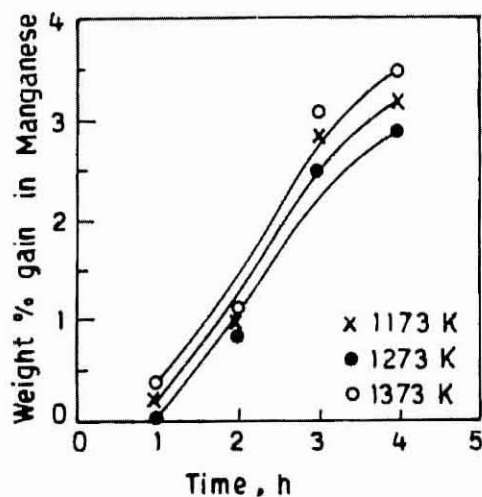


FIGURE 2. Manganese recovery at ambient pressure of carbon dioxide

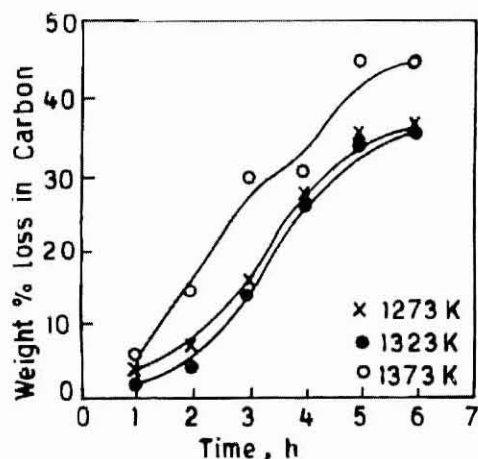


FIGURE 3. Decarburization by carbon dioxide at high pressure

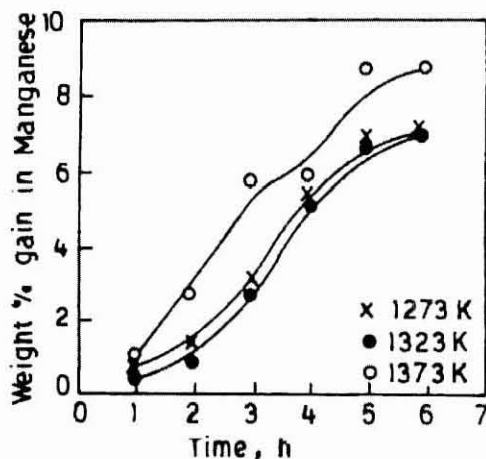


FIGURE 4. Manganese recovery in decarburization by high-pressure carbon dioxide technique

The mass transport of the gaseous products seems to be an important step in the process. This observation is further supported by the results obtained when carbon dioxide was generated *in situ* (Figures 7 and 8). The reacting gas was available at the site itself, and decomposition of calcium carbonate prevented sintering of the solid reactant as well.

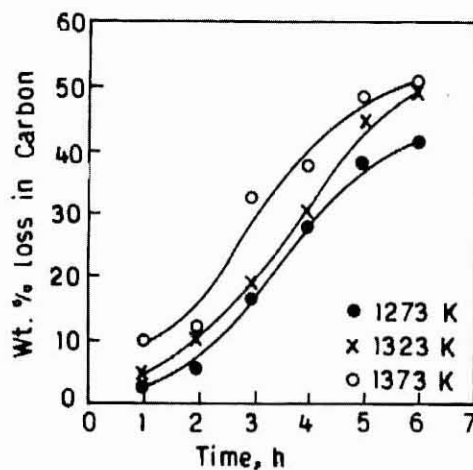


FIGURE 5. Decarburization by high-pressure carbon dioxide plus argon mixture

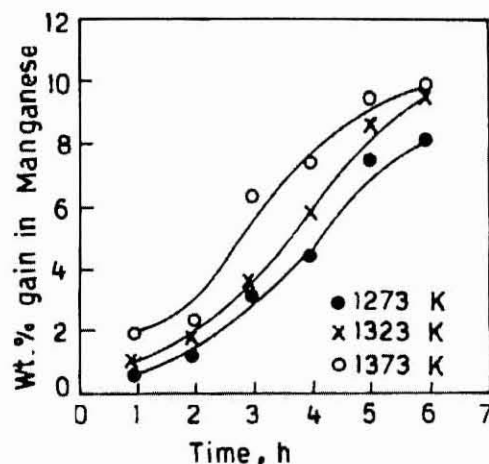


FIGURE 6. Manganese recovery in decarburization by carbon dioxide plus argon mixture

The introduction of the carrier gas (argon) at high temperature assisted in accelerating the continuous removal of carbon monoxide (Figures 5 and 6). The effect of lowering the partial pressure of the product gas (carbon monoxide) is seen in Figure 10. Higher thermal input in all the modes seems to have a beneficial effect on solid-state decarburization.

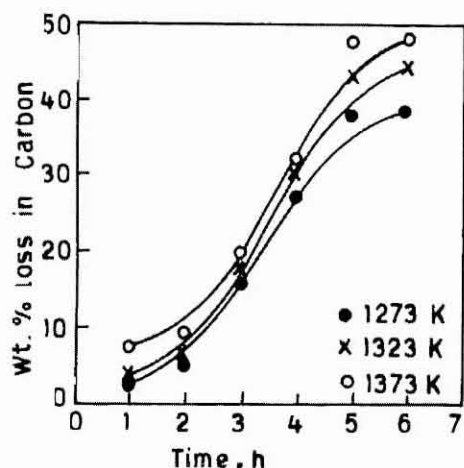


FIGURE 7. Decarburization by *in situ* oxidizer technique

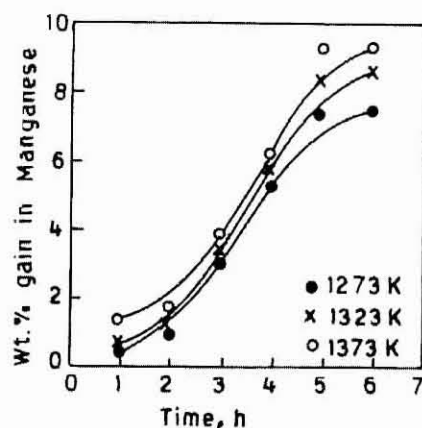


FIGURE 8. Manganese recovery by *in situ* oxidizer technique

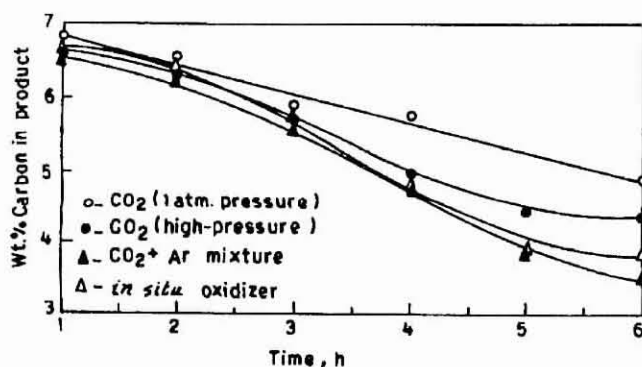


FIGURE 9. Effect of the decarburization technique at 1323 K

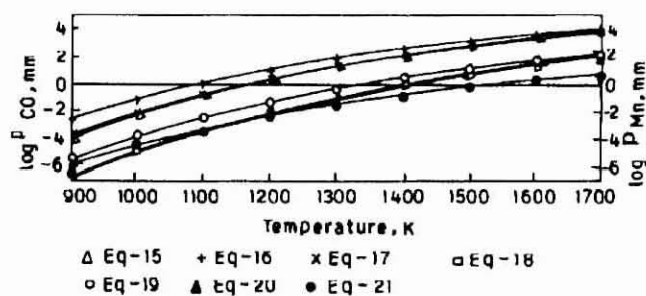


FIGURE 10. Effect of temperature on P_{CO} and the vapour pressure of Mn for various decarburization reactions

The manganese forms a series of carbides ranging¹⁴ from Mn_3C_2 to $Mn_{23}C_6$. Iron is also present in some of these carbides. XRD analysis¹⁵ of the product sample (Figure 11) shows that the solid-state decarburization proceeds via three stages:

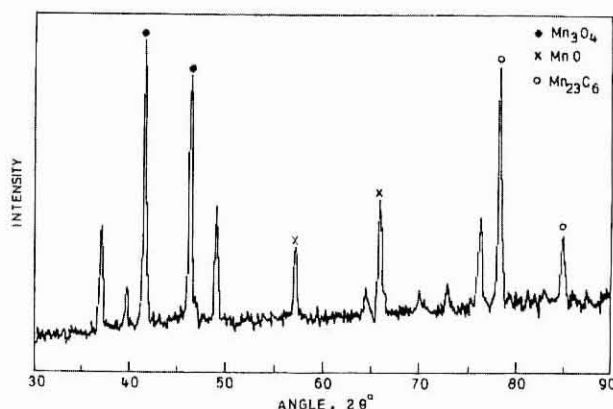
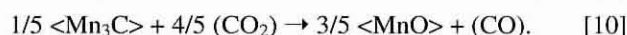
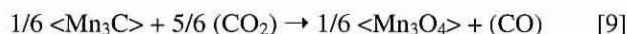
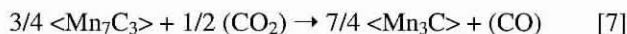


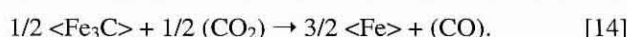
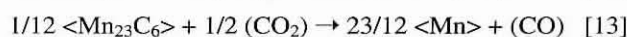
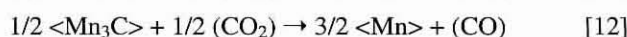
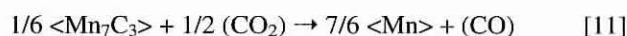
FIGURE 11. XRD spectra of the product after *in situ* decarburization at 1273 K for 6 hours

- (1) transformation of carbon-rich carbides (Mn_3C_2 , Mn_7C_3) into intermediate carbides (Mn_5C_2 , Mn_3C)
- (2) conversion of intermediate carbides into metal-rich carbides ($Mn_{15}C_4$, $Mn_{23}C_5$)
- (3) subsequent refining of metal-rich carbide to metallic manganese.

However, during the first two stages, MnO and Mn_3O_4 were also formed as intermediate products. The major decarburization reactions here are as follows^{16,17}:

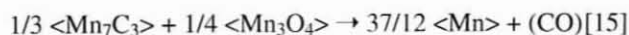


In the third stage, prolonged exposure of the specimen to the stream of carbon dioxide for longer duration at higher temperature leads to the generation of metallic manganese and iron according to the following reactions:

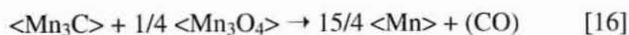


During such decarburization, the formation of the lower oxides of manganese, notably MnO and Mn_3O_4 , seems to

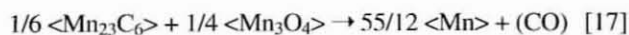
be an inevitable consequence of the reaction. The oxides, once formed, may not offer any resistance to further oxidation, as in the case of chromium oxide¹⁸. As a result, the formation of oxides, rather than the removal of carbon, would be the predominant reaction. This particular situation can be rectified if we consider the reactions in which manganese carbides are converted to metallic manganese by their interaction with manganese oxides:



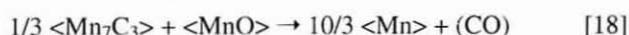
$$\Delta G^\circ = 274,38 - 0,18 T \text{ kJ}$$



$$\Delta G^\circ = 245,77 - 0,17 T \text{ kJ}$$



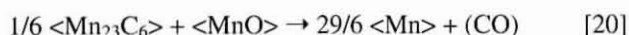
$$\Delta G^\circ = 286,05 - 0,19 T \text{ kJ}$$



$$\Delta G^\circ = 317,01 - 0,17 T \text{ kJ}$$



$$\Delta G^\circ = 288,40 - 0,16 T \text{ kJ}$$



$$\Delta G^\circ = 328,69 - 0,18 T \text{ kJ}$$

$$\log P_{\text{Mn}(\text{mm})} = -12800/T + 8,37. \quad [21]$$

The favourable kinetics for these reactions would invariably occur at elevated temperature. However, there is often the danger of a loss of metallic manganese in the form of vapour phase if a very high vacuum is applied to bring about the above reactions. Figure 10 shows the variation of the equilibrium partial pressure of carbon monoxide and the vapour pressure of manganese metal with temperature. From this it is inferred that, in the reactions where Mn_3O_4 is an oxidizing agent, the equilibrium partial pressure of carbon monoxide is much higher than the vapour pressure of manganese and, hence, if a low vacuum is applied¹⁹, it is feasible to pump out carbon monoxide without the significant loss of manganese in the form of vapour.

Conclusions

Solid-state decarburization of high-carbon ferromanganese by an external and internal oxidizer, i.e. carbon dioxide, has a positive advantage over the conventional and non-conventional techniques followed in the ferromanganese industry. At high temperature and high pressure of carbon dioxide plus argon (carrier gas), better results are obtained, with a product containing about 82,4 weight per cent manganese and 3,39 weight per cent carbon.

Acknowledgment

The authors are highly grateful to Professor S.N. Malhotra and Dr S.G. Sardesai, and to their colleagues at the Thermodynamics Laboratory and the Department of Metallurgical Engineering, for their sincere cooperation and encouragement throughout the course of this work.

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