Oxidation Studies During Decarburization of Ferromanganese

P. J. Bhonde, R.D. Angal*

Department of Metallurgical Engineering & Materials Sciences
Indian Institute of Technology, Bombay
Powai, Mumbai - 400072, INDIA
E-mail : rda@met.iitb.ernet.in
E-mail : pbhonde@hotmail.com

ABSTRACT

Complexities associated with the production process of low-carbon ferromanganese are thus reflected in escalation in its manufacturing cost. Present investigation was hence under taken to explore an alternative simple, economical technique for refining of high-carbon ferro-manganese. Here the impact of various non-traditional decarburizers on the extent of decarburization was studied. The principle behind the process was conversion of carbon rich carbides into metal rich carbide with minimal loss of metal either in the form oxide or vapours.

This process involved utilization of solid decarburizers such as manganese dioxide, manganese carbonate, iron oxide, and calcium carbonate. Also the feasibility of gaseous decarburizer such as carbon dioxide, hydrogen, and water vapour was attempted.

Decarburization process kinetic was studied by analyzing the impact of a few process governing parameters such as the particle size of the reactant, temperature, pressure of the reacting gas etc. The outward diffusion of carbon played a key role. It is expected that, the mathematical model which is under development will benefit in imparting an in depth understanding of the process. It will be useful for predicting the desirable phase and overall rate controlling step whose rate can subsequently be boosted up to increase the decarburization efficiency.

Key Words : kinetics, decarburization, diffusion, carbon, metal carbide, parameters

INTRODUCTION

Low-carbon ferromanganese production is a multistage, multi-furnace, eco-polluting process. It involves high consumption of energy and losses of manganese in the form of slag and fumes [1-3]. Thus this in turn is reflected in its high selling price. Whereas, high-carbon ferromanganese, in which manganese is present as Mn_3C and /or Mn_7C_3 acts as an economic source of manganese [4]. This master alloy is predominantly used for introducing manganese, which not only acts as an austenite stabiliser cum nickel substitute but also improves desirable mechanical properties of alloy steel [5-6]. Presence of carbon in alloy steel, primarily originating from high-carbon ferromanganese, subsequently leads to its failure due to phenomena *viz.* 'sensitisation, weld decay [7].' The present investigation was hence aimed at studying the feasibility of solid-state removal of carbon from its parent source *i.e.* high-carbon ferromanganese.

High temperature oxidation of alloys in carbon containing gases is normally a major problem in industry. Here this concept was used in a positive way to design a practical technique for making low-carbon ferromanganese [8]. It works on the

principle of trans- formation of carbon rich carbides from high carbon ferromanganese to metal rich carbides.

The chosen alloy was subjected to oxidizing environment containing the flowing stream of carbon dioxide under isobaric, isothermal condition for various interval of time. Also hydrogen and water vapour were independently tried for understanding decarburization of the sample under investigation [9-10]. Even kinetically slow, *i.e.* solid-solid homogeneous reactions, between different solid oxidizers such as MnO_2, $MnCO_3$ and pulverized ferro-manganese were attempted to enhance the grade of the final product. However, the overall rate was improved by siphoning out the product gas generated according to the following reaction.

$1/6 <Mn_{23}C_6> + <MnO> \rightarrow 29/6 <Mn> + (CO)$

$\Delta G^o = 325.82 - 0.18\ T$ kJ.

EXPERIMENTATION

The experimental set-up consisted of fabrication of the Kanthal wound resistance heating furnace capable of reaching 1473 K. Main reaction chamber [11] consisted of an impervious, recrystallised alumina tube. It's both the open ends were sealed with indigenously fabricated couplings of stainless steel of AISI 316. They had provision for gas inlet and outlet ports. The chamber was 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 combination of an auto-transformer, solid-state relay and temperature controller cum indicator. The temperature sensor was a calibrated K type chromel - alumel thermocouple. The reactants as well as products were subjected to material characterization studies. These involved elemental analysis by Strohlein apparatus, XRD for phase identification, metallography with optical microscopy and EDAX-SEM for microanalysis of the phases [11].

RESULTS AND DISCUSSION

It was found that, the kinetics of the process was governed by the rate controlling parameters *viz.* particle size of the reactants, temperature, exposure period, vacuum, flow rate and gas composition. Overall increase in the operating temperature, decrease in partial pressure of the product gases or application of vacuum and decreasing the particle size of the reactant resulted in a refined ferromanganese [12-14]. In fact, as illustrated in the Figure - 1, exposure of 5g of 50 micron alloy powder in stoichiometric amount with MnO_2, at 1373 K, under low partial pressure of carbon monoxide *i.e.* 0.001 torr for 5 hours, remarkably brought down carbon from initial value of 6.88 to 2.5 per cent subsequently boosting manganese from 75 to 83 per cent.

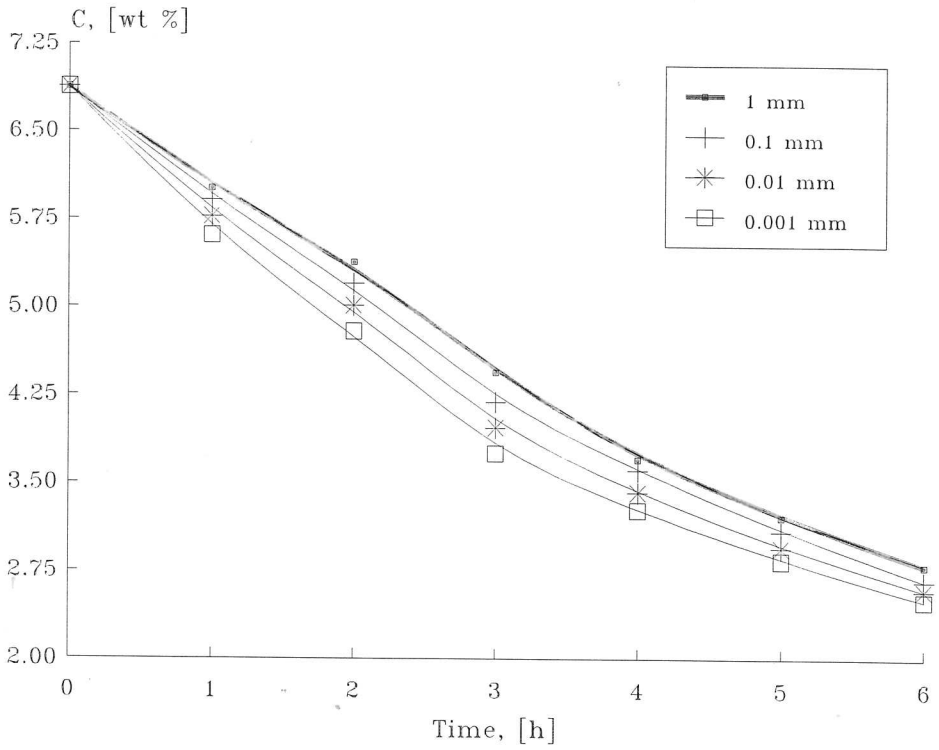

Fig. 1 : Effect of decrease in partial pressure of CO on extent of decarburization at 1373 K

In gaseous as well as solid oxidizer experiments, the alloy showed considerable amount of decarburization along with fairly noticeable quantum of oxidation. Both the phenomena were confirmed from the product topography as well as by X-ray mapping. The XRD results thus obtained are highlighted in the Table - 1.

Table 1 : Phases observed by diffractogram under various experimental conditions [15-16]

Sample Code	Pressure (atm)	Temperature (K)	Particle Size (μm)	Time (h)	Phases detected (Mn oxides/carbides)
a	1	1273	50	1	Mn_2O_3, Mn_7C_3, Mn_5C_2
b	1	1373	50	1	MnO, Mn_3O_4, $Mn_4C_{1.06}$
c	1	1373	50	6	MnO, Mn_3C, $Mn_{15}C_4$
d	10^{-6}	1373	50	6	$Mn_{23}C_6$, $Mn_{15}C_4$, MnO, Mn
e	10^{-6}	1373	100	6	MnO, Mn_3O_4, $Mn_{15}C_4$

These results were also confirmed from identification of the phases in optical and scanning electron microstructures. The EDAX analysis of the same specimen was useful in knowing the exact Mn/O or Mn/C ratio in the various phases observed in the structure [17].

Consequently, under the experimental conditions it was difficult to completely prevent the oxidation of manganese. But, the oxide thus formed *in situ,* if allowed to react further with the remaining manganese carbide(s) will promote in enhancing the metal values [18].

The net mass change in the ferromanganese sample was due to synergistic effect of depletion of carbon and oxidation of manganese. Hence, the decarburization was further studied by application of 'Wagner oxidation model' and 'Unreacted Core model' independently [19-20]. However, this paper has focussed attention on testing the validity of URC model by computing the fractional conversion parameter value for different reaction control mechanisms based on the carbon depletion data. Preliminary experiments in this direction showed that high-carbon ferromanganese particle gradually get transformed into an outer layer consisting of metal rich carbide and oxide with carbon rich carbide core within. Thus the product layer consisting of metal rich carbides plus metal oxides encapsulates the core, which goes on diminishing in dimension with time. In the present investigation one of the reactants as well as the products are in gaseous oxide. During the process they may diffuse counter current wise through the aforementioned product layer. The ash layer offers higher resistance, which builds with time. Hence it gives evidence that, it is an outward diffusion of carbon through layers of manganese oxide/carbide, which will overall govern the rate of the decarburization reaction [21]. Development of mathematical model based on Predominance Area Diagram (PAD) is under progress. This will foster to correlate the experimental findings and predict the existence of various phases under the given operating conditions. With this tool and afore discussed results, in future it may be possible to modify the structure of the oxides by additions of suitable dopants to accelerate the outward mass transport of carbon [22].

CONCLUSIONS

The silent features of the solid-state decarburization technique are it's simplicity of operation without slag formation thereby preventing the corrosion of refractory of the furnace. Besides these, it is inferred that the increase in temperature, decrease in reactant's particle size and pressure has beneficial effect on the extent of decarburization. Overall the outward diffusion of carbon through the ash layer governs the rate of decarburization. It may also be inferred that the, the industrial tonnage scale of this technique can be explored by studying its pilot plant level techno-economic feasibility.

REFERENCES

[1]. Suri, A.K., Gupta, C.K. : **Ferroalloy Technology in India**, 1 st Edn., Mirind Publication (P) Ltd., New Delhi, (1982), pp 9 - 67.

[2]. Downing, J.H. : "Production of Ferro Alloys," **41 st Electric Furnace, Conference Proceedings**, 6 th - 9 th Dec., 1983, Detroit, Book Crafters Inc., Chelsea, Michigan, Vol. 41, (1984), pp 273 - 278.

[3]. Elyutin, V.P., Pavlov, Yu. A., Levin, B.E., Alekseev, E.M. : **Production of Ferroalloys and Electrometallurgy**, *Editor* : Geller, I. & Staff, *Translator* : Shapira, B., 2 nd Edn., The State Scientific and Technical Publication House, Moscow, (1962),pp 96-137, 195.

[4]. Majoulet, J. : "The Uses of Powdered Ferro Alloys," Proceedings of the Metal Bulletin's **1 st International Ferro-**

alloy Conference, Zurich, 9 - 11 th Oct., (1977), pp 19 - 27.

[5]. Touloukian, T.S., Ho, C.Y. : **Properties of Selected Ferrous Alloying Elements, Vol. 3,** 1 st Edn., McGraw-Hill, New York, (1976), p 149.

[6]. Maratray, F.: **High Carbon Manganese Austenitic Steels**, 1 st Edn., Publication of The International Manganese Institute Paris, France, (1995), pp 8 - 94.

[7]. Fontana, M.G., Green, N.D. : **Corrosion Engineering**, 2 nd Edn., McGraw International Book Co., New York, (1978), pp 59 - 60.

[8]. Lai,G.Y.: **High Temerature Corrosion of Engineering Alloys**, 1 st Edn., ASM International, Ohio, (1990), pp 15 - 72.

[9]. Singh, S.K., Deb Roy, T., Abraham, K.P. : "Kinetics of Reduction of Manganese Dioxide Pellets to Manganese Oxide with Hydrogen," *Trans. Ind. Inst. of Metals*, Vol. 27, No. 2, Apr., (1974), pp 87 - 92.

[10]. Shimmizu, S. : "Low-carbon Ferromanganese," Japan Steel & Tube Corporation, 31, 1971, p 656, (Japanese), *Chemical Abstract*, Vol. 79, (1973), p 8568 X.

[11]. Bhonde, P.J., Angal, R.D. : "A New Technique for Refining of High carbon ferromanganese," *Proceeding* of the **1st International Conference on Recent Develop-ment in Ferroalloy Production**, 21st – 23rd Jan., 1993, Bhubaneshwar, India, (1993), pp 59 – 69.

[12]. Garg, S.P., Venkataraman, R., Krishnamurthy, N. : "Thermodynamics of Vacuum Metallurgy," *Seminar* on **Vacuum Metallurgy, VACMET - 92**, 11 th Dec., 1992, B.A.R.C., Bombay, I.I.M. Bombay Chapter & Ind. Vac. Soc., (1992), pp 19 - 54.

[13]. Kamatsu, W : "The Kinetic Equation of the Solid-state Reaction, The effect of Particle Size and the Mixing Ratio on the Reaction Rate in a Mixed Powder System," **Reactivity of Solids**, *Editor* : Swab, G.M., 1 st Edn., Elsevier, new York, (1965), pp 182 - 191.

[14]. Lahiri, A.K. : "Effect of Particle Size Distribution on TG," *Thermochemica Acta*, Vol. 40, (1980), p 289.

[15]. JCPDS : **Inorganic Powder Diffraction Data**, ASTM Publication, Philadelphia, (1989), pp 421 - 468.

[16]. Rutherford, R.T. : "Ferro-Alloy Analysis by X - Ray Fluorescence Spectrometry," *X ray Spectrometry*, Vol. 24, No. 3, May - Jun., (1995), pp 109 - 114.

[17]. Eric, R.H., Burucu, E. : "The Mechanism and Kinetics of the Carbothermal Reduction of Mamatwan Manganese Ore Fines," *Mineral Engineering*, Vol.5, No.7, (1992), pp 795 - 815.

[18]. Jena, P.K. : "Some High Temperature and Low Pressure Metallurgical Reactions of Industrial Importance," *Proceedings of the National Symposium* on **High Temperature Reactions and Processes**, Department of Metallurgical Engineering, K.R.E.C., Suratkal, India, 8 th - 10 th Mar., (1976), pp 63 - 67.

[19]. Kofstad, P : "CO + CO2 Mixture and Diffusional Transport in MnO," *Oxidation of Metals*, Vol. 19, No. 3/4, (1983), pp 129 - 149.

[20]. Szekely, J., Evans, J.W., Brimacombe, J.K. : **The Mathematical and Physical Modeling of Primary Metal Processing Operations**, 1 st Edn., John Wiley & Sons Interscience Publication, New York, (1987), pp 13, 31, 133 - 145.

[21]. Krammer, L.D., Simkovich, G. : "Role of Carbon Dissolution During Manganese Oxidation in CO-CO2," *Oxidation of Metals*, Vol. 6 No. 2, (1973), pp 91 - 100.

[22]. SØrensen, O.T. : **Nonstoichiometric Oxides**, 1 st Edn., Academic Press Inc., New York, (1981), pp 39 - 43, 157, 204 - 218, 220, 406 - 407.