A CONTEMPORARY PROCESS TO ESCALATE $\frac{Mn}{C}$ QUOTIENT OF HIGH CARBON FERROMANGANESE

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ABSTRACT

Manganese imparts numerous beneficial mechanical properties. Hence it finds extensive application in iron, steel and non-ferrous sector. Prevalently, it is incorporated in the form of master alloys i.e. 'ferromanganese'. In India, ferromanganese is mainly the inexpensive and paramount source of availability of manganese.

Various conventional and non-conventional techniques of ferromanganese production have been adopted in past and present. However, these techniques have demerits viz. high refractory, energy consumption, losses of valuables in slag and fumes. Also geographical co-ordinates of the plant restricted the manufacturer to prefer an appropriate process. Accordingly, the industrially implemented methods had reliance on availability of infrastructure, energy, mineral resources, grade of raw material, outlay of labor, environmental compatibility of technique etc.

In view of the liberalized economy and the gap scenario in the supply and demand of ferromanganese, the authors felt it indispensable to explicitly bridge up this vacuum by initially designing a simple energy conserving, eco-friendly, low capital investment technique for decarburization of ferromanganese.

Measurement of the data involved studying the impact of rate governing parameters on the process kinetics. This laboratory scale investigation is expected to escalate the Mn/C quotient of high carbon ferromanganese.

Key Words: ferromanganese, carbon, carbide, decarburization, rate, kinetic

1. INTRODUCTION

Most economical route for production of low carbon ferromanganese either by blast furnace or electric arc furnace comprises of carbothermic reduction of manganese ore. As sited in Table 1, step wise reduction of MnO_2 to Mn leads to formation of several intermediate oxides of manganese viz. Mn_2O_3, Mn_3O_4 and MnO. Subsequently these oxides get reduced to metallic manganese. On similar lines iron oxide in the source also gets reduced in steps.

Table 1: Different type of Mn-O system

Parameter	Metal Mn	Type of Oxide			
		Metal Rich	Intermediate		Oxygen Rich
		MnO	Mn_3O_4	Mn_2O_3	MnO_2
Crystal Structure	Cubic	Cubic	Cubic Spinel	C Rare Earth Cubic	-
Molecular Weight	55	71	158	229	87
O/Mn Atomic Ratio	0	1	1.33	1.5	2
Wt % Oxygen	0	23.9	27.9	30.4	36.7
Oxidation Sequence: Mn → Manganese Rich Oxide → Intermediate Oxide → Oxygen Rich Oxide					

However, during such reduction, thermodynamically, metallic carbides being more stable, the final product is always rich in carbon. Hence, in ferromanganese, carbon is present in the form of carbides of manganese as well as iron. Production of low carbon grade of ferromanganese thus involves refining of such metal carbides by suitable oxidizers.

Since the aim is to achieve maximum decarburization with minimal oxidation, it was imperative to find out the phases that exist under the experimental conditions. This was achieved by considering the binary Mn-C, Mn-O, Fe-C, Fe-O [1] and ternary Fe-C-O, Mn-C-O system [2-3]. Careful analysis of the reported thermodynamic data [3-12] laid the foundation of the study. Literature cited [2], [5] also revealed that, transition element such as manganese forms stable carbides. Therefore, high carbon ferromanganese predominantly contains manganese as well as iron in the form of carbides Mn_3C, Fe_3C and M_7C_3 i.e. double carbide of iron and manganese. From the binary Mn-C and ternary Mn-Fe-C system, the different types of carbides [13-15] likely to be present are as indicated in the Table 2.

Table 2: Different type of carbides in *Mn-C* system

Parameter	Type of Carbide						Metallic Mn
	Carbon Rich		Intermediate		Metal Rich		
	Mn_3C_2	Mn_7C_3	Mn_5C_2	Mn_3C	$Mn_{15}C_4$	$Mn_{23}C_6$	
Crystal Structure	-	Ortho – rhombic	Mono-clinic	Ortho-rhombic	-	Cubic	Cubic
Molecular Weight	189	421	299	177	873	1337	55
Mn/C Atomic Ratio	1.50	2.33	2.50	3.00	3.7	3.87	-
Wt % Carbon	12.7	8.55	8.03	6.78	5.5	5.39	0
Decarburization Path : Carbon Rich Carbide → Intermediate Carbide →→ Metal Rich Carbide ? Metal							

High proportion of carbon in ferromanganese produced by submerged arc furnace process [16] poses numerous problems in its further application as alloying agent. Subsequently these are overcome by decarburization of high-carbon ferromanganese by conventional method which is an evolved process [17]. Alternatively certain non-conventional methods have also been tried, but with little success [18].

The literature survey reveals various techniques were adopted in past and present for decarburization of high-carbon ferromanganese [17]. However, each route had its dependency on the local availability and cost of energy, raw material and labor resources. It is also noticed that, the existing decarburization methods are associated with certain drawbacks viz. loss of metal in slag and fumes. It is thus reflected in the escalating cost of low-carbon ferromanganese. The metal is recovered from slag according to the reaction equation (1).

$$\{Si\}_{metal} + 2\ \{MnO\}_{slag} \rightarrow 2\ \{Mn\}_{metal} + \{SiO2\}_{slag} \qquad (1)$$[1]

It was felt essential to bridge up this gap by finding out an alternative energy conservative and eco-friendly method for decarburization of high-carbon ferromanganese. The investigation was undertaken with the following objectives.

- To study the laboratory scale feasibility of solid-state decarburization of high-carbon ferromanganese to get a semi-refined product.
- Feasibility study of solid-state decarburization by adopting an alternative, non-traditional, gaseous as well as solid oxidizing agent viz. carbon dioxide, manganese carbonate and manganese dioxide respectively.

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[1] !< > = solid phase; { } = liquid phase; ( ) = gas phase.

- To study the process kinetics involving synthesis of the experimental data for understanding the effect of rate governing parameters viz. period, temperature, particle size, pressure on the extent of decarburization.
- Evaluation of the results by application of an appropriate reaction model.

2. METHODOLGY

The work is based on the principle of escalating the Mn/C quotient in high-carbon ferromanganese by exposing the alloy specimen in solid-state, to a suitable oxidizer at high temperature. In high carbon ferromanganese Mn/C weight ratio can be enhanced from about 10 to 80. Accordingly, the experiments were categorized as -

1. Gaseous oxidizer method
   a) Externally supplied gaseous oxidizer
   b) In situ generated gaseous oxidizer.
2. Solid oxidizer method.

Carbon dioxide as gaseous oxidizer was chosen due to following advantages -

At the experimental temperature, the carbon monoxide so formed can be easily removed from the reaction site due to its high diffusivity. The gaseous reactant can also be generated by the thermal decomposition of solid carbonate e.g. manganese carbonate, calcium carbonate.

In the initial stages, carbon dioxide at ambient pressure was generated as an external oxidizer with Kipp's apparatus. Later, it was replaced by CO_2 from cylinder. The X-ray diffraction spectrum of the as received high-carbon ferromanganese showed presence of Mn3C and Mn7C3. The experimentation consisted of exposure of fixed mass (5 g) of powder sample at isothermal condition e.g. 1273 K to the purified CO_2 current at a flow rate of 4.17 x 10-7 m3/s for fixed duration e.g. 4 hours. The sample was furnace cooled to room temperature and the corresponding change in mass of the specimen was recorded. It was further pulverized for carrying out chemical analysis and XRD studies.

Further investigation involved in situ generation of CO_2 by thermal decomposition of the $CaCO_3$ which was mixed in stoichiometric amount (3:1 weight ratio) with the high-carbon ferromanganese powder. Although considerable amount of decarburization was achieved, the overall process was associated with certain shortcomings viz. contamination of the product due to entrapment of CaO which has to be removed by leaching with dilute hydrochloric acid. The contamination problem was solved by replacing $CaCO_3$ with MnCO3 which also had added advantage of comparatively lower thermal decomposition temperature.

Sintering of the reacting mass in external CO_2 method was kinetically unfavorable. This limitation was overcome by replacing gaseous oxidizer with solid oxidizer i.e. MnO_2. Over the previous oxidizers, usage of MnO2 had advantages -

a) It decomposes liberating oxygen [17] at relatively lower temperature.
b) One of the products of decomposition is Mn_3O_4. It is formed even otherwise during decarburization. Its spinel structure facilitates outward mass transport of carbon.
c) As carbon from various manganese carbides present in high-carbon ferromanganese gradually reduces MnO_2, the end product obtained will be rich in manganese.

Since decarburization reactions produce CO which has high diffusivity in CO CO_2 gas mixture, it was imperative that application of vacuum would assist the reactions to a greater extent. Hence further experimentation involved reactions under high pyrovacuum conditions.

3. EXPERIMENTAL SETUP

The experimental setup consisted of fabrication of Kanthal wound resistance heating furnace. It was capable of reaching 1473 K and vacuum 10-6 torr. Main reaction chamber consisted of an impervious, recrystallized alumina tube. Its 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 was evacuated down 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 the power to the furnace through an auto-transformer, solid-state relay and temperature controller cum indicator. Temperature sensor was a calibrated K type thermocouple [19].

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 Mn, Fe, C and Si respectively [20]. Material characterization involved X-ray diffraction analysis using an iron target. Known mass of mixture of high-carbon ferromanganese and manganese dioxide (ratio 1:2 in the form of pellet having aspect ratio unity i.e. height = diameter = 0.5 cm) was placed in a recrystallized alumina boat of known mass. Remaining procedure was identical as aforementioned except in lieu of CO2 atmosphere, the samples were subjected to pyrovacuum treatment.

Similar set of experiments were carried for various particle size of high-carbon ferromanganese, temperature, duration and pressure.

4. RESULTS & DISCUSSIONS

Overall mass loss from each carbide is due to the gasification of carbon to carbon monoxide by oxidizer e.g. carbon dioxide according to the reaction equation (2).

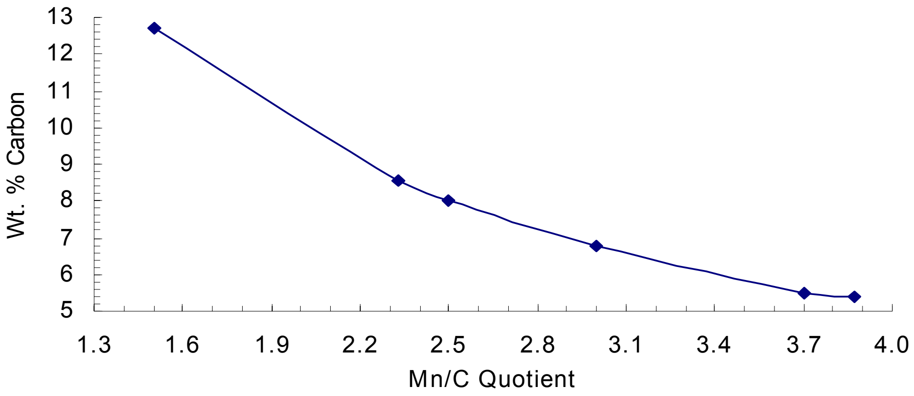

Figure 1: Enrichment of Mn/C quotient during stepwise decarburization of ferromanganese

$$<C> + (CO2) \rightarrow 2\,(CO) \qquad (2)$$

From the results obtained so far [21], it is inferred that such type of decarburization involves, transformation of carbon rich carbides (Mn_3C_2, Mn_7C_3) into metal rich carbides ($Mn_{15}C_4$ $Mn_{23}C_6$) or metal via formation of the intermediate carbides (Mn_3C_2, Mn_3C) [22]. As sited in Figure 1, decarburization at 1273 K indicates escalation in Mn/C quotient. Y co-ordinate represents the weight per cent carbon in each carbide.

However, during such transformation, formations of MnO and Mn_3O_4 as intermediate products seem to be an inevitable consequence of the main decarburization reactions [23-24]. This was also confirmed by indication of the manganese oxides *viz.* MnO, Mn_3O_4 in the XRD spectrum of the decarburized sample. The oxide once formed may not offer much impedance for further oxidation, but it will make the alloy unsuitable for alloy steel production. Practically, it is impossible to completely prevent the oxidation of manganese during decarburization. Hence to enhance the extent of decarburization, only alternative will be to allow to react the *in situ* formed manganese oxide with the remaining as well as the newly formed carbides.

Incidentally, MnO which is thermodynamically most stable oxide plays a key role in decarburization. It is also possible to generate this MnO by including MnO_2 or $MnCO_3$ in stoichiometric proportion with high-carbon ferromanganese powder as one of the constituents of the charge. This being a solid-solid reaction though kinetically slow, it yields a highly refined product. According to the reaction equation (3), decarburization of manganese rich carbide by manganese rich oxide seems to be the most difficult one to get metallic manganese as one of the products in solid-state. Thermodynamically, under standard state conditions, the threshold temperature required to carry out this reaction is about 1910 K, which is well beyond the melting point of manganese.

1/6 < Mn23C6 > + < MnO > ? 29/6 < Mn > + (CO) (3)

Ä G° = 325.8146 - 0.1706 T kJ

But, it is possible to accelerate the forward reaction in solid-state by continuously pumping out the gaseous product *i.e.* carbon monoxide from the reaction site. It is seen that the reduction in pressure thus helps in lowering the theoretical decarburization temperature. Hence it is essential to maintain the experimental pressure lower than that needed for siphoning out CO. However, it has to be optimized such that metallic losses are minimal without affecting decarburization reaction.

5. KINETIC PARAMETERS

Impact of the rate governing parameters *viz.* decarburization cycle period, temperature of decarburization, particle size of the reactants and pressure on the extent of decarburization was studied.

In general, maximum decarburization was noticed over the span of 2 to 5 hours with tolerance of ± 0.5 hour, for a fixed set of parameters *i.e.* temperature, particle size. Decarburization temperature should preferably be maintained around 1373 K for compensating the endothermic reaction heat. It will impart higher driving potential for completion of decarburization reactions leading to about 60 per cent carbon removal. The decarburization with particle size of high-carbon ferromanganese in the range 45 mm to 53 mm was comparatively found more effective than 90 mm o 105 mm. It can be attributed to the availability of larger quantum of reaction sites due to decrease in grain size of the reactants.

Application of vacuum improved the efficiency of the process. Manganese enrichment up to ten weight percent (*i.e.* 82.5 weight per cent Mn in the final product), along with good decarburization could be obtained by subjecting the reacting mass to the vacuum of the order of 0.001 torr.

An attempt was made to understand the oxidation behavior of the high-carbon ferromanganese during solid-state decarburization by externally supplied CO_2 by application of Wagner's oxidation model [25]. Based upon the mass change results, the rate constant and activation energy values for the same were calculated which showed possibility of diffusion controlled mechanism at high temperature regime.

The validity of application of the un-reacted core model was tried. For this the fractional conversion parameter values for different reaction control mechanisms were determined on the basis of carbon depletion data. The best fit was obtained for product diffusion controlled equation indicating it to be the probable rate controlling step [26].

6. CONCLUSIONS

To summarize, the salient features of the solid-state, decarburization technique are it's simplicity of operation without slag formation thereby preventing corrosion of refractory of the furnace. Besides these, it is highlighted that the increase in temperature, decrease in reactant's particle size and pressure had beneficial effect on the extent of decarburization. The impact was seen as an escalation of Mn/C quotient of the product.

REFERENCES

[1] Massalski, B.T.: Binary Alloy Phase Diagrams, Vol. 2, 1st Edn., ASM Pub., Ohio, (1987), p 1574.

[2] Raynor, G.V., Rivlin, V.G.: 'C-Fe, C-Mri, Fe-Mn, C-Fe-Mn', Phase Equilibria in Iron Ternary Alloys, Part-IV, 1st Edn., Published by Inst. of Metals, London, (1988), pp 18 - 21, 43 - 44, 168 - 176.

[3] Raghavan, V. : 'Fe-Mn-O (Iron-Manganese-Oxygen) System', Phase Diagrams of Ternary Iron Alloys, Part - V: Ternary Systems Containing Iron & Oxygen, 1st Edn., Published by Ind. Inst. of Metals, Calcutta, India, (1989), pp 181 - 192

[4] Smith, R.P. : "Equilibrium of Fe-C-Si & Fe-C-Mn Alloys with Mixtures of Methane and Hydrogen at 1000° C", J. Amer. Chem. Soc., Vol. 70, (1948), pp 2724 - 2729.

[5] Hed, A.Z., Tannhauser, D.S.: "Contribution to the Mn-O Phase Diagram at High Temperature", J. Electrochem. Soc.: Electrochemical Science, Vol. 114, No. 4, Apr., (1967), pp 314 - 318.

[6] Benz, K., Elliott, J.F., Chipman, J.: "Solid Phases of the Mn-C System", Metall. Trans., Vol. 4, No. 7, Jun., (1973), pp 1449 - 1452.

[7] idem. : "Phases in the System Fe-Mn-C of the Mn-C System", ibid., Vol. 4, No. 8, Jul., (1973), pp 1701 - 1707.

[8] Nishizawa, Y. : "An Experimental Study of the Fe-Mn-C and Fe-Cr-C system at 1000° C," Scand. J. Metall., Vol. 6, No. 2, (1977), pp 74 - 78.

[9] Turkdogan, E.T.: Physical Chemistry of High Temperature Technology, 1st Edn., Academic Press, New York, (1980), pp 1 - 25.

[10] Terayama, K., Masao, I., Masao, T.: "Phase Equilibria in the Mn-Fe-O System in CO2-H2 Mixture", Transactions of the Japan Institute of Metals, Vol. 24, No. 7, (1983), pp 514 - 517.

[11] Rao, Y.K.: Stochiometry and Thermodynamics of Metallurgical Processes, 1st Edn., Cambridge Univ. Press, Cambridge, (1989), pp 881 - 895.

[12] Davies, R.H. Dinsdale, A.T., Hodson, S.M., Gisby, J.A., Pugh, N.J., Barry, T.I., Chart, T.G. : "MTDATA - The NPL Databank for Metallurgical Thermochemistry", Proceedings of the International Conference on User Aspects of Phase Diagrams, Editor : Hayes, F.H., 25th – 27th Jun., 1990, Joint Research Centre, Petten, Netherlands, Published by The Inst. of Metals, London, (1991), pp 140 -152.

[13] Raghavan, V.: "C-Fe-Mn Carbon-Iron-Manganese", Journal of Phase Equilibria, Vol. 15, No. 4, (1994), pp 421 – 424.

[14] Keshin, K., Persson, L.E. : "A contribution to the Constitution of the Ternary System Fe-Mn-C Isothermal Sections at 1050°,910° and 690° C", Journal of the Iron and Steel Institute, Vol. 174, Sept., (1954), pp 39 - 44.

[15] Levenspiel, O. : Chemical Reaction Engineering, 2nd Edn., Wiley Eastern Limited, New Delhi, (1982), pp 357 - 376.

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

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

[18] Kozak, D.S., Matricardi, L.R.: "Production of Refined Ferromanganese Alloy by Oxygen - Refining of High-carbon Ferromanganese", 38th Electric Furnace Conference Proceedings, Vol. 38, (1981), p 123.

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

[20] Young, J.S. : "The Analysis of Ferroalloys," Talanta, Vol. 33, No., 7, (1986), p 561.

[21] Bhonde, P.J., Angal, R.D.: "Solid-state Decarburization of High-carbon Ferromanganese", Proceedings of the 6th International Ferroalloy Congress, Vol. I, 8th – 10th Mar., 1992, Cape Town, South Africa, Mintek Pub., Randburg, The Republic South Africa, (1992), pp 161 - 165.

[22] Sichen, Du., Seetharaman, S., Staffansson, L.I. : "Some Phase Diagram Aspects of the Mn-C System", Metall. Trans., Vol. 20 (B), Oct., (1989), pp 747 - 754.

[23] Rao, Y.K. : Stoichiometry and Thermodynamics of Metallurgical Processes, 1st Edn., Cambridge Univ. Press, Cambridge, (1989), pp 881 - 895.

[24] Huang, W.: "Thermodynamic Assessment of the Mn-C System", Scand. J. of Metall., Vol. 19, (1990), pp 26 - 32.

[25] Kofstad, P.: High Temperature Corrosion, 2nd Edn., Elsevier Applied Science Publishers Limited, Borking, Essex, (1988), pp 114 - 120, 524.

[26] Bhonde, P.J., Angal, R.D.: "Rate Control Mechanism in Solid State Decarburization of Ferro-manganese", Proceedings of the 10th International Ferroalloy Congress, 1st – 4th Feb., 2004, Cape Town, South Africa, Document Transformation Technologies, Irene, The Republic South Africa, (2004), pp 163 - 172.