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Production of Intermediate or Medium Carbon Ferro Chrome at FACOR

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ABSTRACT

FACOR has foreseen the need to develop the intermediate carbon ferro chrome alloy to meet the demands of alloy and stainless steel manufacturers. The paper describes the decarbonisation of liquid high carbon ferro chrome in an AOD convertor with respect to : (a) Theoretical aspects and fundamentals, (b) Plant and equipment, (c) Process of making intermediate carbon ferro chromium, (d) Advantages of the process to improve the quality with respect to titanium, silicon, hydrogen and nitrogen in intermediate carbon ferro chromium.

Keywords : Ferro chromium, Ferro chrome, Medium carbon, Intermediate carbon.

INTRODUCTION

High speed technology has become the necessity for the modern world to be competitive in the liberalised economy and it has entered the metallurgical fields for steel making and Ferro Alloys production in order to increase the productivity, reduce the production cost, and meet specific quality requirements. The new developments taken place in steel are as follows :

a. Increasing use of electric arc furnaces for alloy steel and stainless steel making.

b. Use of ladle metallurgy for improving productivity and quality and

c. AOD, CLU, VOD secondary refining practices for stainless steel and alloy steel making.

The development of technology for production of stainless steel and alloy steel by Argon, Oxygen, Decarbonisation (AOD), Vacuum Oxygen

Decarbonisation (VOS), Creusot, Loire and Uddeholm (CLU) process etc., permitted the use of high carbon ferro chrome in place of expensive low carbon ferro chrome. With the developments, generally high carbon ferro chrome and scrap are melted in an electric arc furnace to obtain liquid metal with an opening carbon level of 1.8 to 2.0% for refining in AOD and opening carbon of 0.8 to 1.0% for refining in VOD. In order to obtain desired levels of opening carbon i.e., less than 1.0% in the liquid metal for refining in VOD low carbon ferro chrome along with high carbon ferro chrome are used in the proportion of 2:3 FACOR R&D personnel have made an in–depth study and came with a novel idea of development of a new product viz., medium carbon / intermediate carbon ferro chrome with 2–4% carbon, thereby the additions of low carbon ferro chrome can be totally dispensed with. Also the medium carbon ferro chrome can be utilised to produce liquid metal with desired carbon levels for treatment in AOD in order to bring down the consumption of Argon, Oxygen, Fluxes and reductants. This concept was discussed with the major alloy and stainless steel producers in India like Alloy Steel Plant, Durgapur, Mukund Iron & Steel, MUSCO, Bihar Alloy Steel Ltd., Punjab Concast Ltd., Rathi Alloy, BASL, Bhorukka Steels etc., who have got equipments of secondary refining facilities with latest technology. They were convinced with the suggestions, the technological and economic advantages of using medium carbon ferro chromium.

FACOR has foreseen a future, demand for this medium carbon ferro chromium by alloy and stainless steel producers and have developed the technology and established the process parameters for refining of molten (liquid) high carbon ferro chromium, by undertaking systematic investigations over a period of 3 years at their FACOR Works, Shreeramnagar, and Steel Division located at Nagpur. The trials were undertaken in a 4 tone AOD converter. The high carbon ferro chrome was melted at steel division in an induction furnace to enable supply the liquid ferro chromium to converter. The results were highly successful with respect to reduction in carbon content and simultaneously achieving high recoveries of 96% chromium in their end product. During 1989 facilities for production of medium carbon ferro chromium were established at at FACOR, Shreeramnagar (Works).

FUNDAMENTALS AND THEORETICAL CONSIDERATION

The blowing of ferro chromium in an oxygen convertor has been developed for the first time in India by FACOR R&D. Several variations exist in the process with regard to the starting material of the process; the process gases viz., high carbon ferro chromium, charge chromium as starting material, blowing with combinations of oxygen, argon, nitrogen, air steam etc., blowing form different positions in the convertor and blowing under vacuum.

During the process a number of oxidation and reduction reactions take place and thermodynamic data of these reactions is given in the Table 1.

Table 1 : Thermodynamic data of chemical reactions

$$[C]_{1wt\%} + [O]_{1wt\%} \longrightarrow \{CO\}$$
$$\blacktriangle G^{o} = -22470 - 39.8\ T\ \text{Joules}$$
$$[Mn]_{1wt\%} + [O]_{1wt\%} \longrightarrow \{MnO\}$$
$$\blacktriangle G^{o} = -245280 + 109/39.8\ T\ \text{Joules}$$
$$[Si]_{1wt\%} + 2[O]_{1wt\%} \longrightarrow \{SiO_2\}$$
$$\blacktriangle G^{o} = -596400 + 231\ T\ \text{Joules}$$
$$2[Cr]_{1wt\%} + 3[O]_{1wt\%} \longrightarrow \{Cr_2O_3\}$$
$$\blacktriangle G^{o} = -802032 + 271.35\ T\ \text{Joules}$$
$$\{CO_2\} + [C]_{1wt\%} \longrightarrow 2\{CO\}$$
$$\blacktriangle G^{o} = 139860 - 127.68\ T\ \text{Joules}$$
$$4/3\ Al + \{O_2\} \longrightarrow 2/3(Al_2O_3)$$
$$\blacktriangle G^{o} = -1008840 + 154.56\ T\ \text{Joules}$$
$$2\ CaO + (SiO_2) \longrightarrow (CaSiO_4)$$
$$\blacktriangle H^{o} = -125000\ \text{Joules}$$

The activities of various components can be varied and be calculated using the interaction coefficients given in Table 2. These interaction coefficients were determined at 1600°C and it is assumed that these will hold good for actual working temperatures. This table shows the negative interaction coefficient of

Table 2 : Interaction coefficients

Element	O	C	Mn	Cr	Si	Ni
O	-20×10^{-2}	-13×10^{-2}	0	-4.1×10^{-2}	-2×10^{-2}	0.6×10^{-2}
C	-9.7×10^{-2}	22×10^{-2}	–	-2.4×10^{-2}	10×10^{-2}	1.2×10^{-2}
Mn	0	–	–	–	–	–
Cr	-13×10^{-2}	-10×1^{-2}	–	–	–	–
Si	-25×10^{-2}	24×1^{-2}	–	–	32×10^{-2}	0.5×10^{-2}

carbon and oxygen with chromium and will not favour the reduction of chromium under normal conditions. The following reactions highlight the mechanism of the refining process.

Oxidising Reactions

$$[C] + [O] \rightarrow [CO] \quad \ldots \quad 1$$

$$2[Cr] + 3[O] \rightarrow (Cr_2O_3) \quad \ldots \quad 2$$

Reduction Reaction

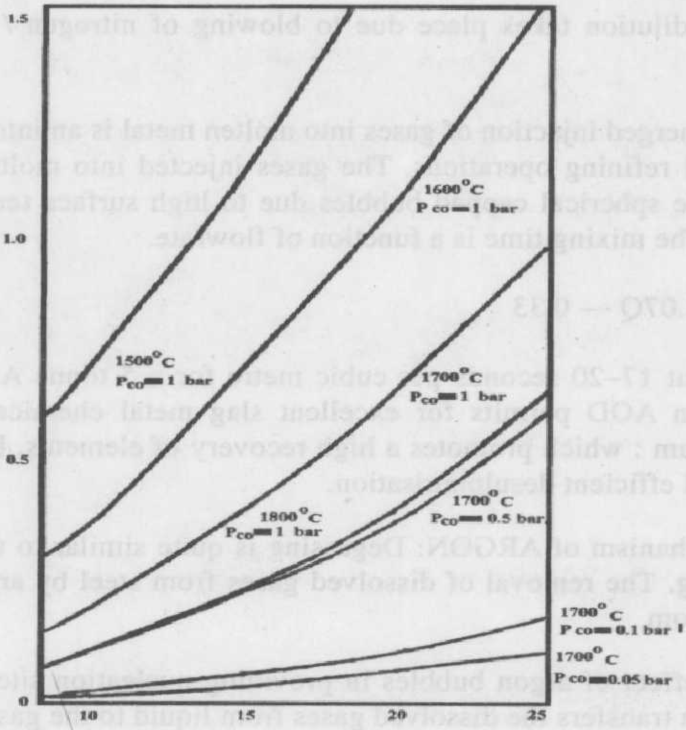
$$(Cr_2O_3) + 3[C] \rightarrow 2[Cr] + 3[CO] \quad \ldots \quad 3$$

The equilibrium constant

$$k_{(t)} = \frac{a^2[Cr] \times P_{CO}}{a(Cr_2O_3) \times a^3C} \quad \ldots \quad 4$$

In conventional process or by simply oxygen blowing into liquid melt of high carbon ferro chrome, oxygen lowers the carbon content and also causes a remarkable chromium slagging which makes the loss of expensive alloying element viz., chromium. To minimise the chromium slagging and have preferential oxidation of carbon, it is necessary to reduce the "CO" partial pressure i.e., by vacuum or diluting by inert gas. The equilibrium constant $k_{(t)}$ describes the equilibrium of two reactions, summarized in Equation (3). Lowering the "CO" partial pressure results in a decreased Cr_2O_3 content of the slag. The temperature dependency of K_t results in the equilibrium being shifted to the right-hand side of the equation 3 i.e., favouring the reduction of chromium.

In the production of high carbon ferro chromium the chromium, oxide is reduced with carbon to chromium at 1240°C and P_{co} = 1 atm. However, the chromium metal reacts with carbon spontaneously at these temperature 1200°C to 1600°C to form carbides $Cr_3 C_2$, $Cr_7 C_3$, $Cr_{23} C_6$, (Cr_4 C). As the temperatures are raised these carbides will become unstable and dissociate into lower carbides. Beyond 1820°C, the chromium exists as metal and not as carbides. Moreover, the smelting process consists of reduction of iron oxide and hence in practice the interference of iron carbide takes place in controlling the carbon in ferro chromium alloys by forming double carbides of $(FeCr)_7C_3$ Table 3 shows the approximate stability ranges for the various products of reduction of Cr_2O_3 and these are related to the pure Cr–O–C system. Therefore it can be seen that the carbides stability decreases with increase temperatures. In substance, with



X–axis → Cr– content in % and Y–axis → C– content in %

Fig. 1 : Equilibria of the Fe–C–Cr–O system is shifted towards lower carbon contents with increasing temperature and lower CO partial pressures.

increasing in temperatures and falling carbonmonoxide partial pressures, the equilibrium can be shifted towards lower carbon content while keeping chromium oxidation low Fig. 1.

Table 3 : Stability ranges for products of reduction of Cr_2O_3

Product	Stability Range (°C)	%C In Product
Cr_3C_2	1150 – 1250	13.3
Cr_7C_3	1250 – 1600	9.0
$Cr_{23}C_6$	1600 – 1820	5.7
Cr	> 1820	0

The AOD process utilises nitrogen/air/argon towards dilution of carbonmonoxide partial pressure. At FACOR, in order to bring down the cost of production, argon is replaced with nitrogen and air. The process is based upon, (1) CO–dilution, (2) mixing and (3) Degassing.

1. The CO-dilution takes place due to blowing of nitrogen / air alongwith oxygen.

2. The submerged injection of gases into molten metal is an intrinsic aspect of the metal refining operations. The gases injected into molten metal form very large spherical capped bubbles due to high surface tension of liquid metals. The mixing time is a function of flowrate.

   $$t = 18.07Q - 0.33 \qquad \ldots \quad 5$$

   It is about 17–20 seconds per cubic metre for a 5 tonne AOD. The good mixing in AOD permits for excellent slag metal chemical and thermal equilibrium : which promotes a high recovery of elements, Fe, Cr, Mn and rapid and efficient desulphurisation.

3. The Mechanism of ARGON: Degassing is quite similar to that of vacuum degassing. The removal of dissolved gases from steel by argon / inert gas results from

   i. The effect of argon bubbles in providing nucleation sites for reactions which transfers the dissolved gases from liquid to the gas phases.

   ii. The improved reaction kinetics resulting from stirring and

   iii. The driving force for these reactions provided by the low partial pressures of CO, H_2 and N_2 in the inert gas bubbles. The CO and argon bubbles absorb H_2, and N_2 as they rise through the bath. In case nitrogen is used instead of argon; in the removal of H_2 is feasible and not nitrogen and it even will result in higher nitrogen content in medium carbon ferro chromium which is required for certain special applications of steel.

Since the process of refining of HCFeCr into medium carbon ferro chrome results very high temperatures which causes severe erosion and corrosion of the refractories, it is essential to control the temperatures suitably without effecting the objectives of lowering carbon and achieving maximum recovery of chromium by selective oxidation of carbon. The slag chemistry is also suitably adjusted in the process.

The total consumption of expensive process gases has to be reduced. This is done by minimising the oxidation of silicon by oxygen and also utilising nitrogen / air in place of argon except where low nitrogen is desired in the final product. The potential chromium loss to the slag has a significant impact on the economic viability of the process. In this process this loss is reduced to a very low level.

Chromium balance over converter :

Basis 100 units of chromium into converter

Balance : Alloy	:	93.00
Slag	:	5.00
Dust, splashing etc.	:	2.00
Total	:	100.00

The heat balance for the process is given in Table 4. The heat efficiency of the process is determined by the portion of the heat provided by the exothermic reactions. In order to utilise this heat within chosen operating margins, additions of coolants viz., M.C., ferro chrome remelts, iron scrap etc., made which facilitates the control of the process thermodynamics and lining wear.

Table 4 : Heat balances in intermediate carbon ferro chromium by AOD process

	Input		Output	
	K.Cal	%	K.cal	%
Metal	3,46,000	41.38	4,03,515	48.25
Heat generated by chemical reactions	4,55,066	54.42	—	—
Formation of slag/ heat content in slag	35,169	4.20	2,12,014	25.35
Radiation & other losses	—	—	83,623	10.00
Heat content in gases	—	—	1,37,083	16.40
Total	8,36,235	100.00	8,36,235	100.0

PLANT AND EQUIPMENT

FACOR ferro alloys division is stituated at Shreeramnagar, 90 Kms. away from Visakhapatnam, the plant has the following components :

a. Three 7500 KVA Submerged Electric Furnaces,

b. One Number 12000 KVA Submerged Arc Furnace,

c. One Number 16000 KVA Submerged Arc Furnace and

d. One Number 8000 KVA Submerged Arc Melting Furnace.

The submerged Arc Furnaces of 12000 and 16000 KVA rating produce mostly high carbon ferro chrome and liquid high carbon ferro chrome, tapped into preheated refractory lined ladles is made available for refining process in AOD converters, installed nearby. The existing 30/15 ton E.O.T. Crane handles all operation of AOD viz., pouring liquid high carbon ferro chrome, handling, teeming and casting operations, additions to the vessel, removal and placement of AOD Vessel as and when required. The AOD plant and equipment for support operations consists of, (i) The Vessels - trunnion ring and associated mechanical drive and Electrical Equipment, (ii) Gas supply and Control System, (iii) Addition Equipment, (iv) Emissions gas ducting and (v) Gas cleaning and Refractory Vessel lining.

The Vessels, Ring and Drive

The AOD stand is designed for removable vessels, while the refractory tearout and reline are taking place, a stand by vessel with new lining is made ready for service; which makes the AOD process available on a continuous basis. The vessel body shape and volume are determined by capacity and factors concerned with ferrostatic heads above the tuyer and the requirements of a certain minimum volume 'Free Board' above slag and metal level. The top conical section is bolted in position to facilitate re-bricking. The center of gravity of the bricked vessel should be below the drive centre line to ensure stability of the plant and safety. Trunnion shafts attached to the trunnion ring are fitted to the bearings which must be capable of carrying not only the dead and live loads imposed by the equipment but also together with their mountings. The bearing should take care of the effects of (a) Trunnion pins misaligned, (b) Expansion and (c) Vibration caused due to turbulence during blowing.

Motor control centre includes thyristor control of DC motor and starters for AC motors.

Gas Supply and Control System

The gas distribution piping for oxygen, argon, nitrogen and dry oil–free compressed air is mounted on a frame work in the valve room. The process gas is fed to the tuyers through rotary joints outside the trunnion shafts and further through central bores in the trunnion shafts to manifolds mounted on the trunnion ring. From the manifold the gases are led to the tuyer through flexible metal hoses and bayonet couplings. The instrumentation and regulation of the process gas flow is installed mainly inside the valve room. A control desk for instrument and control devices is situated in the control room. The gas controls can be manual controls, semi automatic and automatic, where the desired flow rates and mixtures are continuously computed and executed by a central process computer. At FACOR, manual and semi automatic controls were installed.

Pre–Heat Burners

Burners are designed for three requirements.

i. Re–bricked vessel dry out and preheat.
ii. Holding vessel at temperatures when in trunnion rings between heats, and
iii. Preheating of the refractory lined ladle meant for collection of the final melt after processing in AOD separate oil fired burners are provided exclusively for AOD operations in the plant.

Additions Equipment

Periodically, during processing, it is necessary to make materials additions to the AOD vessels as slag formers, slag reduction alloys and coolant additions. These additives are made generally by

i) Manually (by shoelling)
ii) Floor mounted charging car, and
iii) Crane held skip

Overhead addition system is in practice, where AOD installations are of larger capacity greater than 20 tons.

Emissions

During AOD practice, the major emissions are 'CO' gas which is made to burn to CO_2 by mixing with excess air at AOD mouth itself. The solid emissions are both ferrous and nonferrous and the quality of emissions are 5–kg per ton of metal tapped from AOD.

Swingable double mantles hood including supporting structure has been provided. The gas ducting is connected to the bag filter system available, for submerged arc electric smelting furnace, by providing suitable induced draft fans.

Refractory Lining

The refractory lining is exposed to the following effects :

i) Stirring action of the metal and slag by gaseous injection,
ii) Gas pressure variations encountered during charging, decarburisation, reduction and tapping,
iii) Temperature variations during processing activities and between processing cycles,
iv) Chemical reaction with slag and metal.

The refractories used are dolomite bricks or magnesite chrome or mag–carb bricks. The lining life achieved is for 80 heats. "Most important aspect to improve the life of lining is the temperature control which should not exceed 1700°C".

PROCESS

As already highlighted the AOD system consists of refractory lined steel vessel, with the removable conical cover in places, mounted in motorized trunnion ring for tilting and the process controls for injecting the appropriate gas mixtures during the various stages of refining. The vessel is tilted to the appropriate angle for charging, using a transfer ladle containing molten high carbon ferro chrome tapped from ferro chrome smelting furnaces. The sensible heat content of molten ferro chrome has been taken as advantage in refining. After charging, the vessel is tilted to the upright position and the gas injection is begun through bottom–nitrogen alongwith oxygen is injected in desirable proportions to control the temperature during oxidising process.

During the course of processing, the vessel is rotated 90° from the blowing position to a sampling position where metal samples are taken and bath temperatures are measured. At the appropriate time in the heat, while the molten metal is stirred with inert gas, flux materials and reducing alloys and coolants are added to the vessel using an additional chute with vibrating feeder to control the temperature, slag basicity etc. The thermodynamic data and heat requirements are given in Table 5 and 6. The AOD processing steps for refining of high carbon ferro chromium into intermediate/medium carbon ferro chromium are given in Table 7.

While blowing oxygen in initial stages, silicon, is almost totally oxidised and taken in slag which is removed partially and later decarbonisation of the

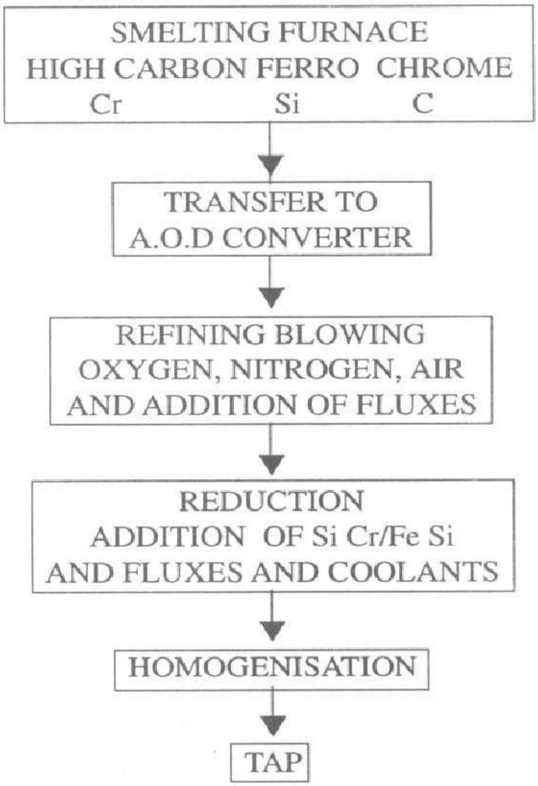
Table 5 : Thermodynamic data

Material	Specific Heat KJ/ Kg / °K	Latent Heat KJ / Kg
Molten Metal	0.84	–
Lime	0.77	1425
Argon	0.52	–
Oxygen	0.91	–
Cr_2O_3	0.69	940
Slag	2.0	–
Ni	0.44	300
Fe	0.46	274
Mn	0.48	266
Si	0.68	1660
Al	0.9	395
C	0.7	–
Cr	0.46	265
MgO	0.95	1942
SiO_2	0.7	182
Fe_2O_3	0.95	866
CaF_2	0.92	915
Al_2O_3	0.78	1070

Table 6 : Heat requirements

Material	1550°C	1700°C	1750°C
Fluospar	2318	2456	2502
Nickel	971	1037	1059
Hot Metal	–	126	168
Chrome Ore	2502	2635	2680
Ferro Silicon	–752	–659	–632
Lime	2600	2715	2753
Aluminium	1768	1900	1950
HC Ferro Chrome	1042	1114	1138
LC Ferro Chrome	842	910	940
HC Ferro Manganese	1130	1200	1230
LC Ferro manganese	750	820	850

Table 7 : AOD processing steps (Temperature, weight and analysis is determined; O_2 and N_2 / air / argon requirements are to be calculated at each stage).



molten high carbon ferro chrome metal takes place. Resiliconisation is carried out at the end alongwith injection of inert gas for effective recovery of chromium from slag to metal and also silicon content in final medium carbon ferro chrome is so adjusted that it is amenable for crushing to the size without resorting to expensive and time cumbersome breaking equipment like pneumatic drop hammers and heavy duty crushers as in case of low carbon ferro chrome.

To summaries the process consists of :

i) Tapping an electric submerged arc furnace for liquid high carbon ferro chrome.
ii) Transferring hot metal to refining vessel i.e., AOD convertor.
iii) Argon (inert gas), oxygen decorbonisation in refining vessel.

iv) Making final additions to refining vessel after blowing.

v) Tapping finished McFeCr from refining vessel and casting in send lined cast steel moulds

vi) The cakes are removed after solidification, cooled, crushed manually, sized, assayed and packed in bags for despatch to end users.

The overall process from the stage of charging liquid ferro chrome into AOD converter to the casting into casting pans will take a cycle time of about 90 minutes. The quantity of molten ferro chrome taken is about 4 tones and finally alloy obtained is also about 4 tons. The specific consumptions per ton of medium carbon ferro chrome containing 2–4% carbon are as follows :

HCFeCr	...	~ 1.1–1.2 tons
Oxygen	...	~ 150 NM^3
Nitrogen	...	~ 30 NM^3
Compressed Air	...	100 NM^3
Ferro silicon/Sr.Cr	...	~ 50 kg
Lime	...	300 kg
Furnace Oil	...	25 lit.

TECHNICAL ADVANTAGES

The AOD operations permit CO dilution, mixing and degassing, thereby, it is possible to achieve the following :

1. The carbon content of HCFeCr can be brought down from about 7.8% to 1–4 %.
2. Selective oxidation of carbon without excessive loss of chromium, manganese etc.
3. Sulphur levels can be brought down below 0.025%
4. To have uniform quality of metal and free from non-metallics. Utilisation of exothermic heat content generated ruing the process, for remelting of FeCr fines.
5. Titanium content can be brought down to less than 0.06% to make FeCr suitable for use in ball bearing steels.
6. The converter can also be utilised for production of other ferro alloys with desired percentages of various elements for specific applications.
7. The AOD process is fast and technically sound with high degree of control and productivity in the production of intermediate / medium carbon ferro chrome.

CONCLUSION

FACOR, could successfully develop and install the AOD operations for production of medium carbon / intermediate carbon ferro chrome, besides meeting specific requirement of alloy and stainless steel producers with respect to carbon, sulphur, phosphorous, titanium, hydrogen and nitrogen. The production started during 1990 and until now produced have about 10,000 tons of medium carbon / intermediate carbon ferro chrome and met the indigenous demand. During this global competition, it is necessary to further improve the operations by providing 100% automatic computer controlled systems to bring down the specific raw–materials consumption and improve the productivity. The computer system should include the important functions namely, Alloy addition, Process temperature and carbon end point control, Slag basicity and chemistry control, Ratio selection, Inert gas selection (N_2 control), Statistical process control, and Vessel positioning.

The benefits will be further reduction in costs of (i) Refractory, (ii) Process gases, (iii) Silicon consumption, and (iv) Shortest heat times.

With the improving productivity and reducing cost of production, the export market for medium carbon / intermediate carbon ferro chrome market can also be exploited.

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