Present status of refractories for ferro-alloy industry

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ABSTRACT

With the growth of steel plant and increased production of alloy and special steels, the demand for ferro-alloys has increased. The present paper describes the refractory practices for producing ferro-alloys.

In the production of low carbon ferro chrome products in the reaction ladles very high temps. are involved. The refractories used in these furnaces are severely eroded and life of the refractories is much low. The paper discusses the typical reasons of refractory wear patterns in these furnaces.

The paper suggests suitable refractories for the production of ferro-alloys like ferro-chrome, ferro manganese, ferrosilicon and also low carbon ferro chrome products.

Introduction

Ferro-alloys are compounds of iron with other metallic or non-metallic elements. They are used as additives for introduction of special properties into steel. The purpose of ferro-alloy addition is to introduce alloying element in steel and to act as decarburiser and degassing agent. It is easier to add the alloying element in the form of ferro-alloys. The type of ferro-alloys used depends on quality of steel

With the growth of steel plants and increased production of alloy and special steels, the demand for ferro-alloys has increased. Development of suitable refractories for smooth and efficient running of ferro-alloy plants is thus essential.

Outline of Process

Ferro-alloys like FeSi, FeMn and FeCr are made by smelting of the reactants in submerged electric furnaces. In ferromanganese, production temperature inside the furnace will be around 1600—1700°C whereas the tapping temperature is 1400°C. The furnace is charged continuously and tapped intermittently. The condition which the refractory has to withstand are to resist high temperature and slag wearout. The typical slag composition is as follows :

MnO	—	30 (%)
SiO_2	—	26 to 30 (%)
CaO	—	14 (%)

The slag is neutral in nature and has a basicity of 1.15.

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The conditions for ferro-chrome production is almost similar but slag is slightly basic in nature. The raw materials for ferro-chrome production comprises mixture of chromite, flux and reducing agents. Inside temperature of furnace is 1900°C whereas outside temperature during tapping is 1650°C. The slag composition is as follows:

Cr_2O_3	—	5 (%)
MgO	—	30 to 35 (%)
Al_2O_3	—	20 to 24 (%)
SiO_2	—	30 to 35 (%)
CaO	—	1 to 4 (%)

Ferrosilicon production is practically a slagless process. The charge consists of quartz, educing agents and iron ore. The composition is selected in such a way that minimum quantity of slag is formed which is about 50 - 100 kg/ton which is negligible.

Refractories in use

In all these submerged furnaces high alumina bricks of 45% Al_2O_3 or above is used as the permanent refractory lining. The actual working layer is composed of carbon lining. Not much refractory problem is encountered in these furnaces when these refractories are used as lining material. The property data of different quality high alumina bricks ranging from 45 % Al_2O_3 to 80 % Al_2O_3 are given in Table - 1. These refractories are indigenously available and can be used as permanent lining material.

The high alumina refractories are manufactured by controlled processing at every stage from suitably selected raw materials to ensure critical properties like high resistance to chemical attack by trickling material, volume stability at high temperature, low open porosity, high compressive strength, good thermal shock resistance and low creep value. The firing temperature of calcined raw materials and also brick firing temperature are controlled in such a way that more coarsely grained mullite is formed instead of finely dispersed mullite so as to increase the corrosion resistance. In the 70% Al_2O_3 and 80 %Al_2O_3 bricks, the superiority in properties is related to the development of intergranular bond like lowering the glassy phase and higher crystalline phases. 70 % Al_2O_3 mullite bricks are manufactured out of fused mullite grains and

TABLE — 1

Properties of High Alumina Refractories available indigenously.

Property		HA-45	HA-54	HA-57	HA-60	HA-62	HA-70	HA-80	HA 80 (dense)	HA-70 (Mullite)	Plastic Refractory
Al_2O_3 %	min	45	54	57	60	62	70	80	80	70	70
Fe_2O_3 %	max	2	1.5	1.5	—	1 5	—	—	—	0.5	—
PCE, SK	min	33	34	35	35/36	35	36	37	37	38	36
B.D , g/cc	min	2.10	2.25	2.35	2.5	2.30	2.70	2.75	2.7	2.60	Grading : (O—6) mm Setting : heat
A. P. %	max	18	22	22	23	24	25	25	22	17	
CCS, kg/cm^2	min	400	450	450	350	250	450	400	400	700	
RUL, 2kg/cm^2 ta°C	min	1480	1480	1500	1450	1500	1470	1470	1600	1700	
Spalling cycles (BRRA)	min	30	30	30	30	8 cycles (1300°C/ water quenching)	30	30	30	30	
Comp. creep, (1700°C/5 hrs with 0 5 kg/cm^2 load)	max	—	—	—	—	—	—	—	—	0.34	

fired at high temperature around 1700°C. These bricks possess excellent properties like very low creep, high thermal shock resistance, high chemical resistance and low porosity.

Out line of manufacture of low carbon ferrochrome products

In the production of ferro-alloys, carbonaceous reducing agents are employed whereas low carbon ferro-chrome products are produced in reaction ladles by treating synthetic slag with metallic reducing agents. For production of low carbon ferro-chrome, a synthetic slag is first prepared by melting a mixture of chrome ore and limestone in an open electric furnace and a highly basic slag containing about 48 % CaO and 24 % Cr_2O_3 is prepared. The synthetic slag prepared from open furnace is then treated with metallic reducing agents in the reaction ladles. The reaction of molten slag from open furnace at 1750 - 1800°C with reducing agents is highly exothermic in nature. This exothermic reaction provides all the necessary heat requirements and even accounting for losses for radiation etc, a temperature of 2000°C is achieved in the ladles. The duration of treatment in the reaction ladles is 40 minutes, but the total time including charging, discharging per heat is about 3 hours. In a ladle capacity of 16 tons, about 2.5 tons of metal is obtained and the rest is basic slag which is wasted. As the density of metal is 7 and of slag 3, no difficulty is encountered during separation of metal and slag in the ladles. Very high temperature of about 1900°C is nvolved in the ladles. Typical composition of slag in the ladles is as follows :

CaO	—	50 to 55 (%)
MgO	—	8 (%)
SiO_2	—	26 (%)

The basicity of slag is about 2.5 which is highly basic in nature.

Refractories in use for low carbon ferrochrome

In the reaction ladles, bricks rapidly erode due to high temperature and slagging reactions. Dense magnesite or magnesite-chrome refractories are generally used as working layer of ladles. In order to decrease high refractory consumption, it is desired to use superior quality refractories in the ladles. The property data of indigenously available basic refractories (for use in reaction ladles is given in Table - 2. These superior refractories can also be used for melting synthetic slag in the open furnace.

The refractories to be used in reaction ladles demand high thermodynamic stability. The higher the temperature, the greater the rate of solution of refractory into slag and greater the degree of penetration of slag components into refractory. Refractory must be able to withstand temperature without developing higher liquid content or showing a high volume shrinkage. This can be achieved by lowering the silicate phases and replacing by highly refractory solid phases.

The conventional basic refractories are silicate bonded. The silicate bond which holds the brick together tends to soften at elevated temperatures. While this complex silicate matrix recrystallises upon cooling making the brick very strong at ambient temperatures, the fact that it is not in a solid state at high operating temps. makes it prone to be attacked and eroded by typical ferro-alloy slag.

The silicate matrix develops high liquid content at hot face. At the high operating temperature, further volume expansion of this liquid takes place and the hot face of the refractory consists of aggregate bonded with large volume of silecious liquid developed at high operating temperature. The penetration of molten slag results further dissolution of brick microstructure. The melt infiltration with the movement of the furnace contents causes corrosion and erosion of the bricks.

It is, therefore, highly desirable to lower down the SiO_2 content to restrict the formation of high amount of liquid at hot face resulting in a liquid bonded aggregate. Also lowering the silica content will restrict the formation of mag-

TABLE — 2

Properties of basic refractories available indigenously

		Burnt Magnesite				Burnt Magnesite-Chrome				Ramming Mass	
		(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(a)	(b)
MgO %	min	87	93	95	91	60	72	70	74	95	86
CaO %	max	—	1.5	2.5	2.5	—	—	—	—	2.3	2.5
Cr_2O_3 %	min	—	—	—	—	10	8	7	8	—	—
SiO_2 %	max	6.5	2.5	1.0	5.5	—	2.5	6	2.5	1.5	7
A. P. %	max	21	23	18	18	23	23	24	21	Grading : (O—4)mm	Grading : (O—4)mm
CCS, kg/cm^2	min	400	400	400	500	250	250	250	350	Setting : Ceramic/ Chemical	Setting : Ceramic/ Chemical
RUL Ta°C (2kg/cm^2)	min	1580	1630	1650	1600	1600	1600	1550	1600		
PCE.SK	min	38+	38+	38+	38+	38+	38+	38+	38+	38+	38+
PLC % (1600°C/2hrs)	max	0.2	—	0.5	—	0.5	0.5	—	0.5	—	—
Spalling, cycles (1300°C/water quenching)		—	—	—	—	—	3	—	—	—	—

nesio-iron-silicate compounds. If the silica contentent of basic bricks are at high level, the silicate matrix will be fluxed by iron compounds. As the slag is rich in lime, whatever forsterite matrix is present will be converted into monticellite. The corrosion reaction can thus be minimised by lowering the SiO_2 content of refractories.

In the reaction ladles, the erosion of refractory lining is very severe. The lining material should withstand the abrasion and chemical attack of trickling material. The proportionate amount of slag formation in the reaction ladles compared to ferro-alloy is very high. With a highly basic slag, magnesia brick is more compatible than magnesite-chrome. Grain growth of periclase is associated with high purity magnesites of notably low silica content to effect ultimate high hot strength bricks. The low silica magnesites show improved resistance to slags rich in lime. Lime forms lower melting silicates with forsterite. It is, therefore, desirable to use magnesites with CaO/SiO_2 ratio above 2:1 so that refractory C_2S is formed with simultaneous reduction in sesquioxides to restrict the formation of low melting calcium aluminates and calcium ferrites. In the magnesite it is desirable to have C_2S matrix and direct MgO-MgO bonding so that this is compatible with the slag. The forsterite matrix is not compatible with the high basicity slag. B_2O_3 content should be limited to low levels so as to get high hot strength properties.

In the production of refined ferromanganese, dense magnesite of low silica content is used where chrome-bearing bricks cannot be used for lining. It has been found that under certain operating condition chrome ore in the brick is reduced to metallic chromium and contaminates the ferro-alloy. Magnesia bricks must be used when these production conditions are present.

Spalling of refractory arises due to thermal fluctuations as well as absorption of metal and slag inside the brick. Absorption results zoned structure because of migration of fusible liquids into cooler zones. The result is increased danger of cracking as a consequence of the deep microstructure densification, weakening of the brick bond and increased susceptibility to subsequent melt infiltration.

Considering the thermal fluctuations magnesite chrome bricks are also used. It has been observed that slag-infiltrated working face of magnesia-chrome prducts is less prone to slabbing than that of magnesia products. Hence to have better spalling resistance properties, conditions favour the use of direct bonded magnesite chrome or co-clinkered Mag-chrome bricks. As the slag involved in reaction ladles is highly basic in nature, this will dissolve the chrome-spinel phase. In such case and specially with the reducing atmosphere, it is preferable to line the ladle with high fired magnesite-chrome bricks of low chrome ore content. Failure due to erosion and also slabbing is minimised by densifying and lowering the porosity and the corrosion reaction is controlled by limiting the silecious components and other fluxes.

The direct bonded Magnesite-chrome bricks of low chrome ore content is manufactured by minimising impurity levels particularly SiO_2 and lime and firing to high firing temps. The bond is a direct joining of magnesia and chome ore grain boundaries and large secondary spinels are formed. Replacing the silicate phase which has recrystallised on cooling by a phase of higher melting temperature gives a product which can better withstand the erosive forces. These refractories are manufactured from high purity periclase and chrome ore and fired to high temperature for the solid state reaction to occur. Major improvement of direct bonded basic brick over conventional silicate bonding are improved hot strength, lower porosity and permeability, better spall resistance, reduction of hot face densification and migration of impurities.

In case of silicate bonded basic brick, frequent temp cycles cross the temp. range where recrystallisation of bonding silicates or mineral phases occur. The direct bonded brick with the absence of those low melting phases show significantly better resistance to temp. cycling. In the direct bonded brick, silicates present as isolated pockets between crystalline interstices contribute to the interlocking nature of main crystals as well as high hot strength.

Magnesite-chrome brick based on co-clinker is available where slag ingress is prohibited due to fine pore size distribution. The markedly improved slag resistance of co-clinker brick compared with conventional direct bonded brick is due to the more uniform spinel phase distribution, lower initial silicate content, lower porosity and permeabilitiy and smaller pore size. The co-clinkered brick densifies at the working face thus reducing the porosity below that obtained during firing of brick. The microstructure of co-clinker products is characterised by low porosity and absence of common pore channels. All the pores occur as isolated voids surrounded by very dense materials. Such microstructure is favourable for increased slag resistance from the physical aspect.

Indigenous Development

Dense magnesite bricks are manufactured from high quality magnesites of very low silica content and of high CaO/SiO_2 ratio. The sesquioxides and B_2O_3 content are restricted to low levels. The bricks are manufactured by maintaining proper granulometry, pressing at high pressure and firing at high temperature around 1700°C. These bricks result in low porosity and high HMOR value. The high hot strength is probably due to distribution of silicates in isolated pockets and more of periclase-periclase bonding.

Magnesites used for manufacture of high fired direct bonded bricks are of low silica and sesquioxides content. The chromite used is of least bursting tendency and oxides like SiO_2, Al_2O_3, Fe_2O_3 are limited to low levels. Bricks are pressed at high pressure and fired to high temperature around 1700°C resulting in low porosity and high HMOR value.

The property data of high fired magnesite and magnasite-chrome and magnesite-chrome based on co-clinker are indicated in Table - 3.

In the bottom and spout of reaction ladles basic ramming material is used. The property data of this material is given in Table - 2.

It is anticipated that high fired pure magnesia dense magnesite-chrome or co-clinker based magnesia chrome products will go a long way in improving the service performance of reaction ladles.

TABLE — 3

Typical properties of high fired basic bricks.

	Magnesite	Magnesite chrome	Co-clinker based Mag-Chrome
MgO %	96.6	72	60.5
SiO_2 %	0.8	2.5	2.0
Cr_2O_3 %	—	8	18.0
A. P. %	17.3	18.0	17.0
CCS kg/cm²	400	300	500
RUL, Ta°C 2 kg/cm²	1650	1620	1620
PCE, SK	38+	38+	38+
HMOR, kg/cm² 1500°C.	85	40	40

Discussion

S. B. Saran, TISCO, Jamshedpur

Q. In what respect the refractories you mentioned are different than those used in the steel melting furnaces ?

A. In the Steel Melting Shops every zone requires different refractory. So you have always to choose and there is a lot of variation in the quality of material that is being used from plant to plant. Some of the refractories that are used in the steel melting shops can be used in ferro alloy furnace also. But one has to go on the plant basis which refractory suits for particular plant and or operation. For instance in ferro chrome and low carbon ferro chrome reaction vessels, the temperatures are very high because of exothermic reactions that are taking place and erosions are very high. Hence service conditions are definitely much more severe than the steel melting shops.

Comments

R. B. Tewari, Universal Ferro & Allied Chemicals Ltd., Tumsar

All the papers were very informative but one aspect of the discussion was conservation of ores. Mr. Sane presented a paper which was for utilisation of rejects and Mr. Sitaramaiah was for utilisation of sub-grade raw material. Now my request is that you were discussing the utilisation of rejects very good. Today it is the crying need that we must utilise it. But user and producer both must work out economics when we are using rejects. What benefits accrue and what are the disadvantages ? Yesterday also there was a paper by Mr. Gupta of Khandelwals. Today also, it has given a fair idea how best they can be used and what are the advantages but I am sure there are disadvantages also. Nobody has tried to bring it out. Regarding utilisation of substandard grade raw material, it has to pass through several stages and at each stage we need either power or metallurgical coke. Unfortunately both are today cost commodity in our country. So we have to see that for conservation or using sub-standard thing we are not overstraining other resources. We have to find out at what cost we are utilising these substandard raw materials. Possibly it might become economical to import these rather than utilising substandard materials. But this is one thing for people to work out, think over and discuss.

D. N. Gupta, Khandelwal Ferro Alloys Ltd. Nagpur.

I have done beneficiation of manganese ore from the point of view of reduction of phosphorus. In IBM where I was serving earlier, we have done a lot of dephosphorisation studies and on the basis of that we had worked out an approximate cost for beneficiated concentrate. It came to be roughly about Rs. 400/- per tonne. Adding another Rs. 250/- per tonne for sintering which we are now getting from Maharashtra Electrosmelt, the cost of dephosphorised concentrate after sintering would roughly come to about Rs. 650/-. Today, for the low phosphorus high grade manganese ores, the landed cost at Chandrapur is about Rs. 550/-. So dephosphorisation is not a very attractive proposition today. But the gap is hardly Rs. 100/- and in the very near future probably it will be very close to each other. Then the idea of using substandard manganese ore with multiple stages of smelting and addition of raw materials and other inputs at two stages probably will not be economical at all and dephosphorisation will be the only solution.

C. N. Harman, FACOR, Shreeramnagar

We hope, along with the technical feasibility, we will also have the economic viability and in process that we discussed here, applicability depends on the economic viability. No investor goes in for investment which is on the face of it not economical. But the technical feasibility proving is also a big part. The paper given by NML shows that with the Indian raw materials we can produce good quality Ca-Si. So technically at least we can be sure that the process is adoptable. So far as economics are concerned, we leave it to the investors who are the best judges.