Application of Magnesite Ramming Mix in Production of Ferroalloy

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1. INTRODUCTION

Several years ago, in China, common magnesite bricks were used for lining electric furnace for medium-carbon ferrochrome, medium-carbon ferromanganese, low (extra-low)-carbon ferrochrome, manganese metal and ferrovanadium by electro-silicothermic process and for lining ladle for low-carbon ferromanganese and extra-low carbon ferrochrome by Perrin-type process. This type of product, however, could not satisfy the need of the high smelting temperature and the intermittent operation because of its low refractoriness under load and poor thermal shock resistance. The furnace or ladle lined with the brick had a short lining life and a high refractory consumption, which restrict the increase in both production efficiency and economic
1.2
results.

Meanwhile, magnesite-ramming mix produced by Haicheng Huayu Refractories Co Ltd. has been successfully used for lining the furnace bottom and ladle for smelting ferroalloy in China. With the application of the ramming mix, the service life of electric furnace or ladle increases by 100 - 150 % and the refractory consumption decreases significantly, leading to an obvious increase in both production efficiency and economic benefits.

1.1 Chemical composition of magnesite ramming mix (see Table 1)

Table 1 Chemical composition of magnesite ramming mix %

MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	Burning loss
≥ 85	6 ~ 8	4 ~ 6	< 0.5	< 1.2	< 0.5

1.2 Physical properties of magnesite ramming mix (see Table 2)

Table 2 Physical properties of magnesite ramming mix

Particle size		mm	6 ~ 0
Bulk density		g/cm^3	> 2.3
Sintering at 1200 °C for	Crushing strength	MPa	10 ~ 12

1200 °C for 3h	Linear change	%	– 0.3
Sintering at 1600 °C for 3h	Crushing strength	MPa	40 ~ 60
	Linear change	%	– 1.8
Major minerals			M C_2F C_4AF C_2S
Bonding phase			Ceramic
Service temperature limit		°C	1900

Note: 1 After sintering at 1600 °C for 3h, the crushing strength of ramming mix can reach that of magnesite brick.

2 The service temperature limit is close to the smelting temperature of ferrochrome or ferromanganese.

3 Mineral structure: M-MgOC_2S-2CaO-SiO_2, C_2AF-4CaO.Al_2O_3.Fe_2O_3, C_2S-2CaO.SiO_2

The sintering of ramming mix begins at about 1200°C when initial strength occurs. It is well sintered at 1600°C with a high resultant strength. After sintering, the primary crystal phase is periclase (MgO), secondary crystal phase is 2CaO.Fe_2O_3 (C_2F) and 4CaO.Al_2O_3 is available in a small amount. The ceramic bonding phase is Fe_2O_3 (C_4AF)2CaOSiO_2 (C_2S). The diffusion and partial solid solution of boundaries between primary crystal phase and boding phase form a stable microstructure at high temperature that is superior to magnesite brick.

The magnesite ramming mix has a good structure and particle size distribution, good sintering property, high service temperature and good penetration-resistance. So the service life of furnace or ladle lined with it can be increased. The other reason for the decreased consumption of ramming mix is that the rammed bottom is easy to be repaired. After the furnace is shut down and the slag and iron retained on the bottom are cleared away, only some ramming repair is needed. There is no need for taking away a lot of worn magnesite brick.

2. APPLICATION OF MAGNESITE RAMMING MIXES IN REFINING FURNACE

The magnesite ramming mix produced by Haicheng Huayu Refractories Co Ltd. has been successfully used in China's 15 ferroalloy furnaces with good results. The following is its application in a 3.5 MVA furnace for medium-carbon ferrochrome.

2.1 Use for lining the bottom of furnace for medium-carbon ferrochrome

2.1.1 Lining process

Adoption by the 3.5 MVA refining furnace (fixed) for medium-carbon ferrochrome, the medium-carbon ferrochrome is produced by the reduction reaction among lumpy silicochrome, chromites ore and lime in the furnace. The bottom is rammed with magnesite ramming mix. The permanent layer and runner are lined with magnesite brick (See Fig.1).

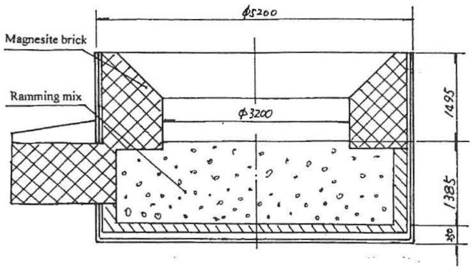

Fig 1 Schematics Diagram of Furnace Bottom Lining

A. Lining of permanent layer and runner

An elastic layer of asbestos board of 10 mm thick and broken clay brick of 100 mm thick for insulation is first laid and then two layers of clay bricks are laid as a permanent layer. The runner is lined with magnesite brick, which enters the furnace wall 345 mm.

B. Ramming of bottom with magnesite ramming mix

The magnesite ramming mix is rammed on the permanent layer and is made firm by plate-type vibrator when every 7 tons of mix (about 150 mm thick) is rammed to achieve a density of 2.7-2.8 g/cm^3(about 120 mm thick). After this, a rough surface is made using spike-tooth harrow and another layer of mix is rammed.

When the thickness of rammed bottom reaches 1370 mm, the first layer of magnesite brick for wall is laid. Then, 2 tons of ramming mix is laid to make the rammed layer reach 1490 mm thick.

The wall brick is laid as normally and a slope is rammed with ramming mix along the junction of wall and bottom.

2.1.2 Supplying power and baking furnace

Lumpy lime and silicochrome are uniformly spread on the bottom to start arcing after the wastes are cleared away. And then, the mixture of chromite ore and lime and the silicochrome alloy are added into the furnace one by one. The electrically baking of freshly lined furnace is carried out according to the operation regulations on power load and consumption. The surface layer of rammed mix is guaranted to be sintered at 1600 °C for more than 3 hrs to form a hard sintered layer of high compressive strength. After tapping the first heat, the bottom is inspected to make sure that it is in a good condition. The normal production can be carried out after that.

2.2 Analysis on sintered bottom

The 3.5 MVA refining furnace worked for 119 days with the following results: operation of 1338 heats, a total output of ferroalloy of 4580 tons, daily output of 38.5 tons, an increase in daily output of 3.5 tons, unit power consumption for smelting of 76 KWh, and 260% increase in the lining service life. After the shutdown and 8 days' natural cooling, the retained slag and alloy are cleared away, the furnace is dissected and the sample is taken for analysis.

2.2.1 Visual examination on samples

As smelting goes on, the slag erosion of bottom becomes more serious and the bottom, electrode tip and bath descend. The amount of molten alloy retained in the furnace increases with the descending of melting pit despite the position of tapholes is progressively adjusted down.

It is observed that the lower edge of alloy lump formed from molten alloy retained in the furnace enters the magnesite ramming mix 1100 - 1200 mm. The thickness of lump ranges from 10 to 30 mm. The ramming mix at the bottom is well sintered and has four distinct layers: corrosion layer, sintered layer, transitional layer and original layer.

The corrosion layer is adjacent to the bath and 10 - 20 mm thick. The layer cracks into gray pieces or white powder as the natural cooling goes on.

The sintered layer, take the wall for example, is dark brown and dense. The thickness varies from about 40 mm at the upper part to 150 - 200 mm at the lower part as the smelting goes on, the high temperature field descends and the exposure to high temperature is prolonged.

The transitional layer is semi-sintered and brown. The thickness is about 50 mm at the upper part and 80 - 100 mm at the lower part.

The original layer is light brown.

2.2.2 Slag erosion

With the descending of bottom-sintered layer, the changes in chemical compositions are shown in Table 3.

The chemical erosion of rammed bottom by slag is more serious around the electrode because the temperature at the end of electrode is higher than the other positions. The corrosion of wall near the electrode (slope bottom) is less serious.

Table 3 Chemical compositions of samples from sintered layer

Position of sample	SiO_2	CaO	Fe_2O_3	MgO	Al_2O_3	Cr_2O_3
Ⅰ-1	6.55	7.01	5.89	76.77	0.77	3.78
Ⅰ-2	8.74	15.50	2.72	72.00	1.15	0.28
Ⅰ-3	4.37	10.49	4.10	80.28	1.22	0.30
Ⅱ-1	1.97	10.26	7.15	78.27	1.05	0.13
Ⅱ-2	2.18	13.18	5.05	77.55	1.17	0.15
Ⅱ-3	2.62	12.24	3.78	81.37	0.99	0.29
Original brick sample	1.14	6.75	5.30	85.05	0.72	—

Note: Ⅰ - refers to the bottom near the electrode tip; Ⅱ - refers to the wall opposite to the electrode.

It can be seen from the Table 3 that the content of CaO in sintered layer is up to 10 -14%, a big increase compared with that in the original brick. The content of SiO_2 also increases significantly, with a content of 6 - 8% in the sintered layer near the electrode from 1.14% in the original brick. The above-increases show that the slag of high basicity formed during smelting can penetrate into the magnesite ramming mix. The silicate phases of high melting point formed by reaction of CaO and SiO_2 at high temperature such as C_2S+C_3S can protect the bottom.

2.2.3 Structural analysis on sintered layer of bottom

The analysis shows that the sintered layer consists predominantly of MgO, $2Ca.Fe_2O_3$, $2CaO.SiO_2$ and so on. The periclase has a larger particle size and is surrounded by bonding phases including C_2F etc.

The major mineral in the corrosion layer is MgO, $2CaO.SiO_2$. $2CaO.Fe_2O_3$ can be occasionally seen. The boundaries of the periclase grains are filled by C_2S. The corrosion layer is in contact with molten slag and molten alloy which may penetrate into the boundaries of periclase grains. The metallic beads in the crystal may be the product of reduction of oxides in solid solution (Mg.Fe)O.

2.2.4 Analysis on the erosion of magnesite ramming mix

The erosion of bottom mainly occurs in the interface between sintered layer and molten slag, i.e. in the corrosion layer. On one hand, bottom is slowly eroded with the entering of CaO_2 and SiO_2 in the low-basicity slag. On the other hand, the bonding phase $2CaOFe_2O_3$ decomposes at high temperature to form the solid solution (Mg.Fe)O and the C_2S and C_3S of high melting point, which inhibit the diffusion of molten slag and the erosion of MgO, being the main reasons for long service life of bottom.

2.3 Refractory maintenance

2.3.1 In order to reduce the slag erosion of furnace bottom, a reasonable slag basicity is necessary. The slag basicity (CaO/SiO_2) of 1.7 - 1.8 is desired for smelting medium-carbon ferrochrome. The typical slag compositions are as follows.

CaO	SiO_2	MgO	FeO	Al_2O_3	Cr_2O_3	CaO/SiO_2
48.55	28.23	7.89	0.89	7.75	3.97	1.72

2.3.2 In order to reduce the washing of furnace bottom by molten ferrochrome retained in the furnace, tapping holes should be lowered with the thinning of bottom caused by erosion.

2.3.3 Compared with the largely increased bottom life, the service life of wall is short and becomes a critical factor in extending the service life of furnace. Therefore, maintenance and repair of wall should be strengthened and it is advisable to repair the worn area of wall with lime and magnesia material.

2.4 Technical and economic results from using rammed bottom

2.4.1 The magnesite ramming mix has been successfully applied in seven 3.5-6.3 MVA electric refining furnaces for medium-carbon ferromanganese, medium-carbon ferrochrome and extra-low carbon ferrochrome in Jilin Ferroalloy (Group) Co Ltd. The good application and increased economic results have been obtained.

In 605# electric furnace (3.5 MVA) for medium-carbon ferrochrome, lining life was about 45 days and 110t bricks were needed when it was lined with magnesite bricks. The life, however, increased to about 90 days and only 24t ramming mix was needed when it was rammed with magnesite ramming mix. The refractory consumption decreased from 50 kg/t to less than IO kg/t.

In 105# electric furnace （3.5 MVA ） for medium-carbon ferromanganese, the lining life of magnesite brick lining was about 45 days. When it was rammed with magnesite ramming mix, the life increased to 88 days.

In 505# electric furnace (6.3 MVA) for extra-low carbon ferrochrome, the service life increased from 25 days of magnesite brick lining to 51 days of magnesite ramming mix.

The adoption of magnesite ramming mix to furnace bottom has led to an increased lining life, a decreased consumption of refractory, power and manpower caused by shutdown and maintenance. Thus, the yield of ferroalloy has increased and a good economic result has been achieved.

2.4.2 The magnesite ramming mix was trial-used in the bottom of 1.0MVA electric furnace for medium-carbon ferromanganese in Emei Ferroalloy (Group) Co Ltd. The rammed bottom of 924 mm thick worked safely for 130 days and 1142 heats of medium-carbon ferromanganese were smelted. The erosion thickness was about 800 mm Polar Regions of electrode and no serious damage to the bottom occurred. After repairing the bottom with 10t magnesite ramming mix, repairing the worn wall and building tapping holes, the furnace resumed its operation.

In 202# (3.5 MVA) electric furnace for medium-carbon ferromanganese, the campaign reached 120 days when its bottom was lined with the magnesite ramming mix but was just 50 - 60 days when the bottom was lined with magnesite bricks before. The similar results were also achieved in the furnace for ferrovanadium when the ramming mix was used in the bottom.

2.4.3 The service life of synthetic magnesite ramming mix reached 469 heats in 3.0 MVA electric furnace for medium-carbon ferrochrome in Hunan Ferroalloy Factory, an increase of more than 200% compared with the figure when magnesite bricks were used.

2.5 The application of magnesite ramming mixes in tilting refining furnace

The magnesite ramming mix was used in electric furnace for medium-carbon ferromanganese and manganese metal and good results were achieved in Zunyi Ferroalloy (Group) Company. Its 222# furnace (1.8 MVA) is a tilting-type refining electric furnace for medium-carbon ferromanganese. Both the bottom and wall of bath were lined with magnesite ramming mix (see Fig. 2). When the wall of bath is rammed, a brick mould should be built beforehand. 18t and 19t ramming was used respectively for bottom and bath.

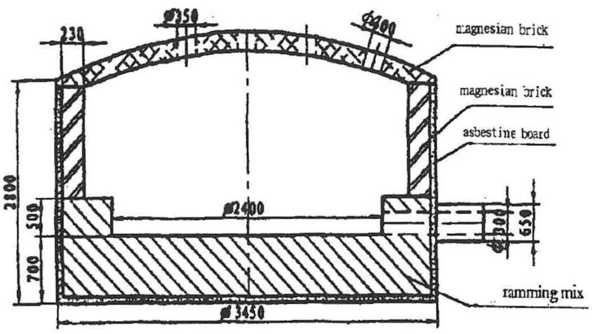

Fig. 2 Schematic Diagram of Rammed Lining

In order to achieve a good sintering of surface layer of lining and to meet the operating conditions for medium-carbon ferromanganese, blends are loaded before baking and starting-up after the lining is finished and the smelting time is increased by 1.5 hours. Starting from the second heat, the smelting is conducted in accordance with the normal conditions. The campaign of furnace with magnesite ramming mix reached 60 - 70 days, a big increase from 38 days when the magnesite brick was used. When magnesite brick was used, 35 t brick was consumed for one campaign but only 8 - 9 t magnesite ramming mix is needed for one campaign when the magnesite ramming mix was used. The application results of both types of products are shown in Table 4.

Table 4 Application results of magnesite brick and magnesite ramming mix

Lining material	Output of alloy t	Power consumption KWh/t	Mn recovery %	Refractory consumption t /campaign	Unit consumption kg / t
Magnesite brick	1060	1198	7405	20.3	35
Magnesite ramming mix	1640.6	1141	1141	≤ 8	< 9

After a successful application of magnesite ramming mix in 1.8 MVA electric refining furnace for medium-carbon ferromanganese in Zunyi Ferroalloy (Group) Co., the product has found a satisfactory application in 3.5 MVA furnaces for medium-carbon ferromanganese and in the furnaces for manganese metal in the company. The highest lining life of tilting furnace for manganese metal is 344 heats, average life 234 heats, an increase of nearly 90 heats compared with that of magnesite brick lining.

3.THE APPLICATION OF MAGNESITE RAMMING MIXES IN LADLE

According to Perrin-type process for extra-low carbon ferrochrome presently adopted in China , chromite ore and lime are first melted in refining furnace and then the molten is poured into a ladle. After this, liquid or solid silicochrome alloy is added into the ladle and thus extra-low carbon ferrochrome is produced through exothermic reaction of silicon oxidization. The process of adding liquid silicochrome alloy is adopted in Hengshan Ferroalloy Factory and the process of adding solid silicochrome alloy in Jilin Ferroalloy (Group) Co. and Shanghai Shenjia Ferroalloy Company. Jilin Ferroalloy (Group) Company began to use the magnesite ramming mix for lining ladle in 1999 and has obtained satisfactory results.

3.1 Ramming and lining of ladle

The ladle works under the condition of sharp temperature changes. Therefore, the service life of magnesite brick lining is low due to spalling. The figure is about 50 heats in Shanghai and just 38 heats in Jilin. The low lining life caused by severe working conditions is a difficult problem in extro-low carbon ferrochrome production. After the successful application of the magnesite ramming mix to the bottom of its refining furnace, Jilin Ferroalloy Company is planning to apply the ramming mix to the ladle linking with a 6.3 MVA electric furnace. The schematic diagram of ladle lining is shown in Fig.3.

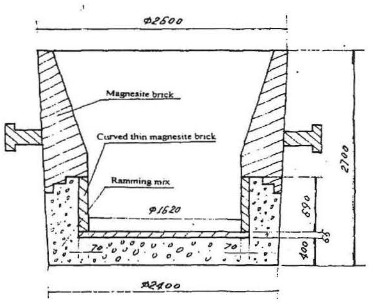

Fig. 3 Schematic Diagram of Ladle Lining

3.1.1 The bottom of ladle is wholly lined with magnesite ramming mix and the work is carried out in two times.

3.1.2 A level layer of standard magnesite brick is laid in the central part on the rammed bottom. After this, a circular brick mould is built on the magnetsite brick for ramming the ladle wall. The building of mould is carried out along with the ramming of wall.

3.1.3 When the preset height of rammed wall is reached, magnesite bricks are laid up to the top end.

3.1.4 The rammed wall is naturally cooled or baked by hot slag to remove the water of mortar binder. Then, the ladle can be put into operation.

3.2 Maintenance and repair of ladle

3.2.1 In general, the sintering of magnesite ramming mix is completed after baking of more than 2 hours at 1550 - 1600℃. Although its working temperature is as high as 1920 - 1970℃, the ladle lining is soaked with melt which is the high temperature just for 20 - 30 minutes every 1 hour or more, resulting in a thin sintered layer. Therefore, the cold slag and alloy retained on the bottom or wall should not be prized when the ladle stands idle or the cold slag and alloy are dumped. Otherwise, the original layer will come out and the lining will separate from the ladle shell.

3.2.2 The ladle nozzles at both sides should be alternately used to pour hot liquid. Otherwise, the wall and bottom at one side is worn more seriously than the other side because of the mechanical washing by molten slag and chemical attack.

3.2.3 In order to make efficient use of the magnesite ramming mix, slag on the bottom should be completely cleared away to reveal the original rammed layer and then the wall is cleaned from bottom to top. After this, the magnesite ramming mix and magnesite brick are laid.

3.3 The application results of magnesite ramming mix in ladle

The service life of ladle lined with magnesite ramming mix and brick is 145 heats without any repairs. If the ladle lining is properly repaired, the ladle can continue to work for more heats.

The lining life of ladle for smelting extra-low carbon ferrochrome has been being kept at above 100 heats in Jilin Ferroalloy (Group) Company. The consumption of refractories has been 20 kg per ton of alloy, which is 80 – 100 kg lower than that in the case of magnesite brick. The increased lining life has brought the company good economic benefits.

4. CONCLUSIONS

4.1 With high-CaO magnesite as the main raw material and the addition of high-activity iron oxides, the magnesite ramming mix produced by Haicheng Huayu Refractories Co Ltd. has a reasonable chemical compositions, mineral composition and particle size distribution. The mix can obtain a good sintering at 1550 - 1660℃ thanks to the presence of bonding phases C_2F and C_2S. Meanwhile, the product has a high application temperature limit.

Under the operating conditions of furnace or ladle for smelting ferroalloy, RO i.e. solid solution (Mg.Fe)O and minerals C_2S and C_3S in the sintered layer hinders the diffusion of molten slag into the sintered layer and then the abrasion of the sintered layer.

4.2 Under the working conditions, the magnesite ramming mix has a dense sintered layer, a transitional layer and a plastic original layer combination of which results in the bottom and wall of furnace or ladle having a good integrality and a good thermal shock resistance. Thus the service life of furnace or ladle increases by a big margin.

4.3 The dry ramming process is simple and easy to master. The worn lining is easy to be repaired which contributes the safe operation of smelting facilities. Moreover, the prolonged lining life by using the magnesite ramming mix is beneficial to an increase in production efficiency and a decrease in production cost.

4.4 The magnesite ramming mix has been successfully and widely used in electric furnace for steel making, refining furnace and ladle for smelting ferroalloy with good results. China's ferroalloy producers that have refining facilities will use magnesite-ramming mix within the year 2000.