THEORY AND APPLICATION OF MAGNESIA RAMMING MATERIAL IN FERROALLOY REFINING FURNACES

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ABSTRACT

Magnesia ramming materials have been widely used in China instead of magnesia bricks as furnace lining materials of ferroalloy refining furnace. The paper introduces the development of the ramming material, recounts its chemical composition, physical property and application characteristics. Because of its high MgO contents and fine sintering property, the ramming furnace bottom has the properties of good refractory, monolithic construction and thermal shock resistance. The changes in mineral composition and furnace tearout characterization show the reasons for the bottom's long service life. The obvious benefits are widely achieved, the annual saving cost in refractory is about 2 millions US dollars.

1. INTRODUCTION

The most outstanding technological progress in Chinese ferroalloy industry in recent several years is the transformation of refractory materials. Vitality and economic benefit are brought to the Chinese industry by the replacement of magnesia brick with ramming material. Since the first medium carbon ferrochromium furnace adopted ramming material in Jilin Ferroalloy Company Limited, all Chinese large and medium ferroalloy enterprises have used the new materials in their refining furnaces. All achieved increased lining life and decreased and refractory consumption.

2. DEVELOPMENT OF RAMMING MATERIAL

Magnesia ramming material is unshaped refractory, which is shipped in bulk bags and made into a seamless lining body at the worksite. No pre-shaping or pre-casting is required.

The development of magnesia ramming material for ferroalloy furnace is based on the use of unshaped refractory used in steel making electric furnace.

During the 1960s and 1970s, the sintering additive of first ramming materials was iron oxide. This decomposed at high temperature, changing from high valence iron to low valence iron [1]. The following reaction of Fe_2O_3 will occur in the presence of molten iron:

$$Fe_2O_3+Fe_{(l)}=3FeO \quad (1)$$

or

$$Fe^{3+}+Fe_{(l)}=2Fe^{2+} \quad (2)$$

The melting point of FeO is 1 355°, the temperature of liquid phase is lower, the consumption of the bottom is mostly the lost of the material. Therefore, the furnace bottom is eroded quickly and service life is shortened.

After 1980s, with the introduction of large-size furnace with high power and super-high power, unshaped refractory also entered into the Chinese market. In order to better utilize the material to meet the need of higher power smelting, a new series of ramming materials for furnace bottoms were manufactured. These

new materials consists of MgO-CaO-Fe_2O_3; chosen by laboratory testing and field trials. Their physical properties meet or exceed world standards for the same materials, and the material is generally less expensive.

The sintering additive for the new ramming material is dicalcium ferrite C_2F. Before service, the synthetic additive is manufactured and the reaction is:
$2CaO+Fe_2O_3=2CaO\cdot Fe_2O_3$

Being a high temperature sintering additive, C_2F not only aids in sintering by forming liquid phases during the in-situ reactions, but also reacts to forming solid solution silicate with high melting point. This characteristic microstructure enables the ramming material to have good sintering character and erosion resistance.

By the end of the 1990s, for ferroalloy refining furnace, especially for medium, low and extra-low chromium, the temperature is 100°C~ 200°C higher than that of steel making furnace. Furthermore, some conditions, such as a strong reducing atmosphere and high ferroalloy melting point are harsher than that of steel making furnaces. Cooperating with ferroalloy companies, some scientific research institutions and refractory companies conducted research to improve the material′s properties so that it could be used successfully in ferroalloy refining furnaces. This resulted in a series of ramming materials for ferroalloy furnace bottom.

3. CHARACTERISTICS OF RAMMING MATERIAL IN FERROALLOY FURNACE

The chemical composition and physical property of ramming material in furnace bottom are listed in Table 1.

Table 1. Chemical composition and physical property of ramming material on furnace bottom.

Code Index	GYDL- T83	HYDL- T85	HYDL- T84	HYDL- T86
1.Chemical composition				
MgO	83	85	84	86
CaO	6~7	7~8	6~8	7~8
Fe_2O_3	5~6	4~5	5.5~6.5	3.8~4.5
SiO_2	<1.2	<1.0	<1.2	<1.0
Al_2O_3	<0.6	<0.4	<0.6	<0.3
I.L	<0.5	<0.5	<0.5	<0.5
2.Physical property				
Size/ mm	6~0	6~0	6~0	6~0
Bonding character	Ceramic	Ceramic	Ceramic	Ceramic
Compression strength/ MPa				
1 200℃ 3 h	>13	>10	>12	14
1 600℃ 3 h	>45	>40	>45	>50
Linear change rate / %				
1 200℃ 3 h	+0.2	+0.3	+0.3	+0.4
1 600℃ 3 h	-2.0	-1.8	-2.0	-1.8
3.Temperature limit / ℃	1800	1900	1850	1950

3.1 High Smelting Temperature

The composition of ramming material is usually CaO 6% ~ 7%; Fe_2O_3 below 5%; MgO over 85%. The properties of fire resistance are improved also. The working temperature of ramming material nears the actual smelting temperature of low carbon ferrochromium, which is 1850 ℃~1950 ℃.

3.2 Good Sintering Property

In order to make up for the possible decrease in sintering because of the decrease of Fe_2O_3 and increase of MgO, we made a technological innovation. Micro-powder and super fine powder techniques are applied in the production of the ramming material. Because fine powder composition made adjustment, the sintering properties are improved very much, and there is no obvious shrinkage in early sintering period with less liquid phase, which makes the sintering strength increase greatly. The compression strength of sample can be 40 ~ 50 MPa after 3 hours sintering at 1 600 ℃.

3.3 Homogeneous And Rational Structure

The ramming material for ferroalloy is produced by calcining high MgO magnesite and super fine high activity iron oxides, and then adjusting the size distribution.

Fe_2O_3 reacts with CaO in the dry ramming material thoroughly in the process of calcining and forms (C_2F) which distributes homogeneously (Figure 1).

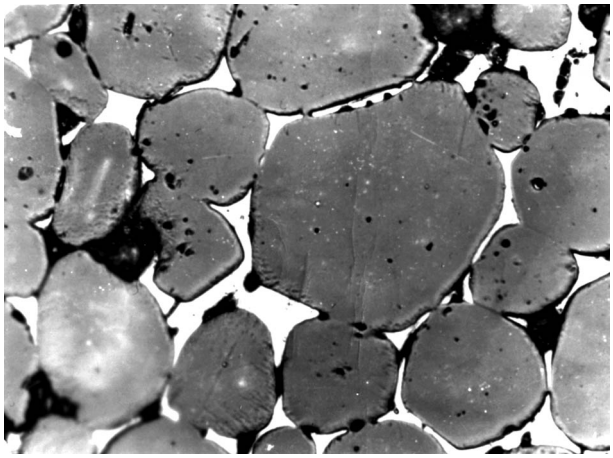

Figure 1. Periclase (M)-the dark grey round particle; grey white C_2F homogeneously distributed in the lattice.

4. MINERAL COMPOSITIONS AND EFFECT OF C2F

4.1 Mineral Composition

The mineral composition of ramming material includes M (MgO) C_2F($2CaO \cdot Fe_2O_3$) C_2S($2CaO \cdot SiO_2$) C_4AF($4CaO \cdot Al_20_3 \cdot Fe_2O_3$) . The rates of each mineral in HYDL-T85 are showed in Table 2.

Table 2. Mineral composition %.

Mineral	M	C_2F	C_4AF	C_2S
HYDL-85	86.7	7.4	1.2	3.7

From Table 2 we can see the primary crystal phase is periclase (M) about 86. 7%, the second crystal phase is (C_2F) about 7. 4%, which is greater than C_4AF and C_2S(as shown in Table 2). C_2F is the main ceramic bonding phase of ramming material.

Figure 2 is the X-ray diffraction analysis curve. There are two obvious crest lines. A is the main crystal phase MgO manual line. B is the second crystal phase $2CaO \cdot Fe_2O_3$ manual line. The manual lines of C4AF and C_2S are not obvious, so it proves that the contents of C_4AF and C_2S are very low.

Since the C_2F is the major ceramic bonding phase, it is essential to analyze the behavior and change of C_2F in smelting, so we can better understand the wear mechanism and discover the reason of long bottom life.

4.2 The Effect Of C2F

It is reported in the literature that the melting point of C_2F is 1 449 ℃ and it decreases to 1 100℃ in the presence of liquid iron. So the sintering agent of dry magnesia ramming material is C_2F. There are usually small amounts of SiO_2 and $A1_2O_3$ in dry magnesia ramming material, so the temperature of liquid phase emerging will be lower than 1 100℃ according to the authors opinion.

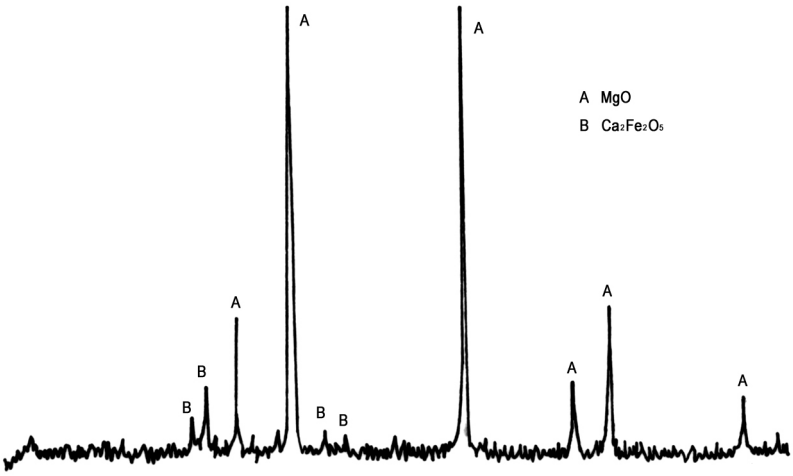

Figure 2. X-diffraction analysis curve of ramming material.

During the furnace operation, the liquid phase forms locally at 1 100 ℃ and the ramming material begins to sinter. With the increase in furnace temperature, the amount of liquid phase increases and the operating surface gradually sinters and solidifies. The whole layer, sinter layer, formed at 1 500 ℃ when the sintering process finished. This is the first effect of C_2F sintering at high temperature.

C_2F in the liquid phase forms a high melting point new phase after phase transformation at high temperature, which increases the stability of ramming material. This is the second effect of C_2F which makes magnesia ramming material superior to magnesia brick. From the CaO-FeO and MgO-FeO phase diagrams we can see when liquid FeO formed by C_2F disintegration comes in contact with large amounts of magnesia, FeO will be absorbed by magnesia to form a solid solution. With MgO absorption, the melting point gradually increases. At the same time, CaO will react with SiO_2 in the ramming material or in the slag and to produce high melting point silicates of C_2S and C_3S which increases the stability, corrosion resistance and washing resistance.

4.3 Furnace dissection analysis

To prove the unique effect of C_2F, furnace bottoms and ladles were analyzed on tear-out. The results are discussed in other papers so the following is only an abstract.

The layers can be seen clearly from the samples taken. They are usually divided into 4 layers: operating layer, sintering layer, transiting layer and unchanged layer.

The operating layer also called wear layer has a thickness of 10 ~ 20 mm. This layer is in contact with the metal pool. With a decrease in temperature, it will gradually become white briquette or gray white powder.

The Sintering layer is dark brown and very dense. As smelting progresses, the position of the high temperature zone moves down. The thickness of sintering layer widen gradually from top to bottom of the furnace. The thickness in the wall is 40 mm, and the thickness in the bottom is around 100 ~ 150 mm.

The transiting layer is between the sintering and unchanged layer and is in a half sinter state. The thickness is about 50 ~ 80 mm and is brown in color. The unchanged layer is light brown color.

The erosion effect mainly takes place in the operating layer, and so it is the focus of research. The results of X - ray diffraction are in accordance with microscope analysis. The powder samples in operating layer are mainly M, C_2S and C_3S. The C_2F disintegrates completely and only the trace of residue can be seen. Many silicates such as C_2S fill up the periclase grains, which are surrounded by silicates and are in contact with molten slag. The periclase grains are gradually worn and the particles become smaller and more rounded. Some edges are not as clear as in the sinter layer (figure 3).

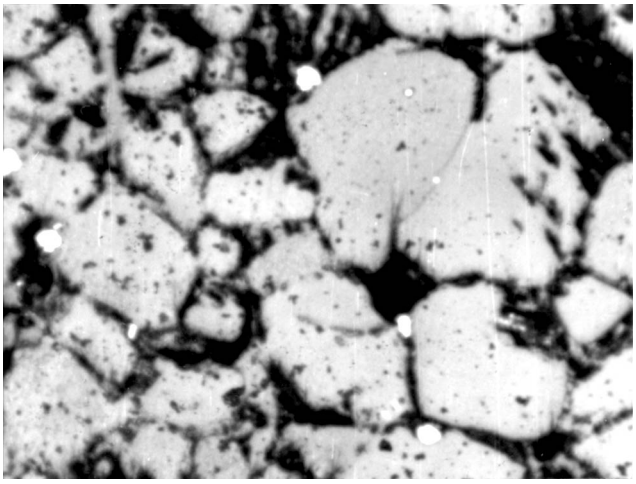

Figure 3. Microscope photo of erosion layer.

The metal drops of different sizes in samples result from contact of the operating layer with the metal pool and the reducing atmosphere in furnace (Figure 4). The larger metal droplets in the grain surface may be the result of liquid alloy penetration. The metal drops in periclases grains are very fine and distributed randomly. These droplets are the reductive products of iron and magnesium oxides in (Mg • Fe) O solid solution.

The research on dissection samples further confirms the viewpoint that C_2F will form two new phases with high melting point after the finish of sintering process and disintegrating at high temperature. C_2F plays an important role on the behavior of synthetic material in high temperature and decides the stability and durability of furnace bottom.

5. ANALYSES OF EROSION MECHANISM OF FURNACE BOTTOM

The details of erosion samples from different furnaces and different positions of the same furnace may be not the same by analyzing the dissectional samples. But the regularity of erosion is the same. The study of the regularity can make better understanding the wear mechanism and discover the reason of long service life.

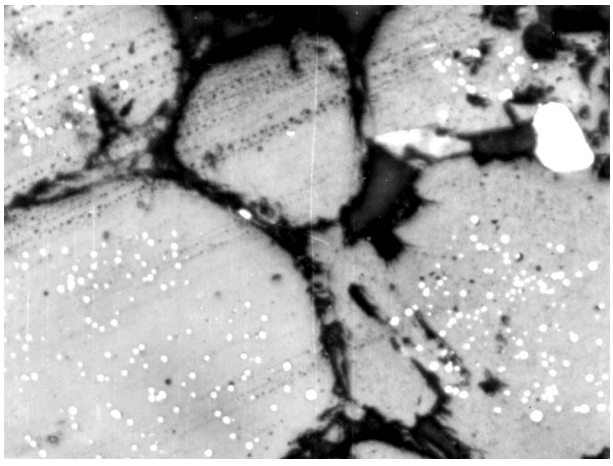

Figure 4. Metal drops in periclases grains of erosion layer.

The density of unshaped ramming material sinter results from the proper grain size distribution, ramming density, temperature and time. After the starting of the furnace, liquid phase forms in the operating layer at 1 200 ℃ and the sinter begins. At the beginning only a small amount of C_2F dissolves in the crystal lattice of periclase and forms a solid solution to improve the sinter ability of the material. When the temperature rises further, C_2F disintegrates, liquid FeO is assimilated by periclase and forms (Mg •Fe) O while CaO forms calcium-rich liquid or forms C_2S with SiO_2. The sintering process finishes when the original material transforms from MgO + C_2F to RO + C_2S.

The sinter layer is very dense with no permeability, which prevents the penetration of molten slag so the bottom of furnace is protected.

The main composition of slag contacting with the operating layer are CaO and SiO_2. With the penetration of molten slag, the surface of the periclase is worn and CMS-C_3MS_2 bonding phase are formed. These phases have low melting points causing the furnace bottom to gradually wear. The loss of ramming material mainly due to the dissolution of Periclase solid solution, so the process of dissolution is very slow.

A C_2S-rich zone can be observed in the operating layer near the sinter layer[2]. This layer improves the high temperature properties (C_2F fills in the periclase) and can also prevent the erosion of silicate liquid. The layers immigrate to the lower part when the reaction takes place and CMS-C_3MS_2 formed. During the furnace maintenance and furnace bottom cool up to 400 ~ 500 ℃, the phase transform from β-C_2S to γ-C_2S with 12% volume inflation. This makes the structure of the operating layer not dense and turns into white powder. However the thickness of this layer is only 10 mm, the stability of furnace bottom material is not affected.

Comparing with magnesia brick lining, the bottom of the furnace is monolithic rammed, and has superior thermal shock resistance. The phenomenon of bottom turnover with magnesia brick lining is avoided. The consumption of refractory is decrease and the service life of the bottom is prolonged.

6. CONCLUSIONS

The unique microstructure and good physical properties of the new ramming material make the application in ferroalloy refining furnace more successful and its use is spreading quickly.

At present, all ferroalloy refining furnaces in China adopt this new material and technology. The service life of furnace linings is increased, consumption of refractory is decreased and the operating rate is increased, which results in good technological and economic benefit to each ferroalloy company.

Three other furnaces including a medium carbon ferromanganese furnace in Zunyi Ferroalloy Company, a high carbon ferrochromium furnace in Hunan Ferroalloy Company and a high carbon ferrochromium in Jilin Ferroalloy Company are in operation now. Emei Ferroalloy Co. is preparing the application of this ramming material in their high carbon ferromanganese production.

7. REFERENCES

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