Influence of Fused CaZrO$_3$ Addition on Properties of Chrome-free Castables for RH Degassers

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Abstract. This thesis considered specific operating conditions of RH degassers, using corundum and spinel as the main raw material, adding proper micropowder and the efficient compound water reducing agent, discussed the influence of fused CaZrO$_3$ addition on RH degassers used chrome-free castable's properties, which includes the castable's strength, permanent line rate, wear resistance and performance of the slag resistance. The results showed:

1. Adding proper fused CaZrO$_3$ can improve the strength of castable and wear resistance;
2. With the increase of the content of CaZrO$_3$, volume density of castable declined slightly, apparent porosity increases, the line rate increased obviously;
3. With the increase of the amount of CaZrO$_3$, slag erosion resistance of castable declined;
4. From the perspective of the comprehensive performance of castable, fused CaZrO$_3$ suitable addition amount of 2 ~ 4%.

1. Introduction

RH degassing vacuum cycle method is more popular among steel plants with its advantages as good degassing performance, taking off less heat from molten steel, wide application scope, flexible and reliable operation compared with a variety of other refining outside the furnace method[1]. Therefore, RH vacuum refining is widely applied by big steel plants. However, the demanding environment of RH refining forces its lining to use the direct binding or combine magnesite chrome brick, but using magnesite chrome based refractory will produce poisonous hexavalent chromium. Thus, chrome-free refractory materials are widely researched in present domestic universities, enterprises and research institutes. The general research is in corundum-spinel system since this system of materials is of high strength, good abrasion resistance, high temperature volume stability, excellent thermal shock resistance and good resistance to slag erosion, etc[2]. But the class and conditions of iron and steel smelting are complex in RH degassers. Materials of corundum-spinel system is no longer the ideal material facing the great thermal stress change and high basicity (R quartile 2.5) of the molten slag erosion. Therefore, it becomes the focus of attention as how to make corundum-spinel chrome-free material that adapts to RH refining environment, especially with higher resistance to erosion of high basicity slag. The characteristics of fused calcium zirconate are microstructure uniformity, high
strength, good resistance to chemical and mechanical attack. Pollution free and environmental friendly, it becomes ideal alternative raw materials to magnesium chromium, magnesium and aluminate spinel[3]. This paper based on corundum-spinel system, using fused CaZrO$_3$ and as the research object, purposed to improve its abrasion resistance, spalling resistance and resistance to high basicity slag erosion, thereby to improve the service life of chrome-free refractory in RH degassers.

2. Experimental

2.1 Raw materials in experiment

Using densely corundum ( grain size of 5~3 mm ), 3~1 mm, 1~0 mm, ≤0.074 mm fused white corundum, 1~0 mm, 325 mesh fused spinel, CA-80 cement, active alpha Al$_2$O$_3$ micro powder as the main raw materials, added 325BS fused CaZrO$_3$, the physical and chemical indexes are shown in table 1.

| Raw material                  | $\text{Al}_2\text{O}_3$ | $\text{Si}_2\text{O}_3$ | $\text{CaO}$ | $\text{MgO}$ | $\text{Fe}_2\text{O}_3$ | ZrO$_2$ |
|-------------------------------|--------------------------|--------------------------|---------------|---------------|--------------------------|---------|
| Densely corundum              | 98.31                    | 0.21                     | 0.03          | 0.02          | 0.15                     | -       |
| Fused white corundum          | 99.51                    | 0.22                     | 0.03          | 0.02          | 0.30                     | -       |
| Fused spinel                  | 77.56                    | -                        | -             | 20.35         | -                        | -       |
| Activated alumina             | 98.90                    | 0.23                     | -             | -             | 0.08                     | -       |
| CA-80 cement                  | 77.89                    | -                        | 19.12         | -             | -                        | -       |
| CaZrO$_3$                     | -                        | -                        | 26.90         | -             | -                        | 70.84   |

Table 1. Chemical compositions of main raw materials( wt %)

| compositions                  | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | $\text{FeO}$ | $\text{CaO}$ | $\text{MgO}$ | $\text{TiO}_2$ | MFe | P | S |
|-------------------------------|---------------|--------------------------|--------------------------|---------------|---------------|---------------|---------------|-----|---|---|
| Content( wt %)                | 10.4          | 23.69                    | 5.46                     | 4.69          | 34.64         | 14.6          | 0.36          | 1.36 | 0.13 | 0.029 |

Table 2. Slag compositions ( wt %)

2.2 Recipe of experiment

| Raw material                  | 1# | 2# | 3# | 4# | 5# | 6# |
|-------------------------------|----|----|----|----|----|----|
| Fused corundum (5~0mm)        | 76 | 74 | 72 | 70 | 68 | 66 |
| Fused spinel (325BS~1mm)      | 10 | 10 | 10 | 10 | 10 | 10 |
| Active alumina                | 10 | 10 | 10 | 10 | 10 | 10 |
| CA-80 cement                  | 4  | 4  | 4  | 4  | 4  | 4  |
| CaZrO$_3$ (325BS)             | 0  | 2  | 4  | 6  | 8  | 10 |
| additive                      | 2.2| 2.2| 2.2| 2.2| 2.2| 2.2|

Table 3. Recipe (wt%)

2.3 The experiment process and performance testing

2.3.1 Experiment process

Weighs all sorts of aggregates, powder, binding agent and water reducing agent in proportion according to the recipe. then pour the materials into mortar blender. Dry mixing for 1~2 minutes until well distributed and then slowly add right amount of water to wet mix for 2~3 minutes to reach the standard of molding. Put mixed wet material quickly into the sample mould (160×40×40mm) which
was set in advance. Charging during the vibration process until there is little small bubbles and the pulp appears. Keep the castable in mould for 24h and then demould to measure its body size. Maintain the demould sample in room temperature for 24h. Put the sample in electrical drum wind drying oven in 110°C for 24 hours for drying. Finally after drying of sample perform 1100°C×3h, 1500°C×3h heat treatment.

2.3.2 Performance testing

1. Adapting the three point bending method, according to GB/T 3001-2000, measure the normal temperature flexural strength; According to GB/T 3997.2-1998, measure the samples' cold modulus of rupture and cold crushing strength.
2. Adapting the Archimedes drainage method, according to GB/T 2997-2000, measure the samples' apparent porosity and volume density.
3. Measure the samples' linear expansivity rate after heat treatment according to GB/T 5203-1993.
4. Measure the samples' wear resistance according to GB/T18301-2001 test methods.
5. Slag resistance ability test is performed using static crucible method, put proper amount refining ladles slag into crucible, analyze the eroded crucible by dissecting its fracture surface after heat treatment in 1550°C for 3 hours.

3. Results and discussion

3.1 Effect of CaZrO<sub>3</sub> on strength of castables

![Graph](image_url)

**Figure 1.** Influence of CaZrO<sub>3</sub> on strength of castables

Figure 1 shows, when CaZrO<sub>3</sub> addition amount of 4%, the sample flexural strength and compressive strength achieves maximum, than the strength of sample without CaZrO<sub>3</sub> has improved significantly. But, when the addition of calcium zirconate quantity within 4 ~ 10%, with the increase of MZ addition amount, the strength of sample has declined, this is mainly because: (1) the castable in shape, with the increase of CaZrO<sub>3</sub>, water content increasing, the liquidity is reduced, cause 110°C x 24 drying the samples after the porosity increases, the intensity is reduced, but just because the reason of forming the strength reducing trend of small;(2) 1100°C for 3 h sample, because the sample did not happen a lot of chemical reaction, so it was; and the strength of the 110°C trend;(3) samples at
1500 ℃ sintering, a small amount of CaO and Al₂O₃ reaction to generate CA₆ in matrix, the compactness of material increase, the microstructure was optimized. So when CaZrO₃ addition amount was 4%, the strength of the specimens significantly higher than that of the original, but CaZrO₃ in 4-10% range, along with the increase of the content of CaZrO₃, CaO content is increased, so the generated CA₆ volume also increased significantly, leading to sample, loose structure, expansion, resulting in significantly reduced intensity[4]. From the perspective of the intensity of the sample, addition amount of 4% of CaZrO₃ achieve more ideal effect.

3.2 Influence of CaZrO₃ on castables’ permanent linear change

As seen in figure 2, under 110 ℃ and 1100 ℃, with the increase of the content of CaZrO₃, permanent line rate of castables is not obvious, but the sample under 1500 ℃, with the increase of the content of CaZrO₃, permanent linear change of castables is obvious increase, the main reason is that under the condition of high temperature, along with the increase of the content of CaZrO₃, CaO content increased, so the generated CA₆ volume also increased significantly, causing sample quantity increase. From the permanent line rate of castables, when the addition amount of 2% of CaZrO₃, sample volume is more stable.

![Figure 2. Effect of CaZrO₃ on permanent linear change of castables](image)

3.3 Influence of CaZrO₃ on castables’ wear-resisting

According to the national standard, set the 100×100×30 mm standard sample's test surface vertically to sand blasting tube, blow the wear medium (black silicon carbide) through the gush arenaceous pipe on to sample using compressed air and then measure each sample's wearing volume. Through calculation, the wear-resisting results is shown in figure 3.

![Figure 3. Wear-resisting index/cm³](image)
Figure 3. Influence of CaZrO\textsubscript{3} on castables' wear resistance
As seen from the figure 3, for the amount of CaZrO\textsubscript{3} from 2\% to 4\% range, its wear resistance is better than the same CaZrO\textsubscript{3} (0\%); When the content of CaZrO\textsubscript{3} was 4\%, the wear resistance of sample is best, its wear resistance increases by about 33.5\% than before. Main reason is the system of a small amount of CaO at high temperatures and matrix of Al\textsubscript{2}O\textsubscript{3} reaction CA\textsubscript{6}, its microstructure was optimized, thus improving strength and wear resistance increased. But the content of CaZrO\textsubscript{3} in 6\%~10\% range, along with the increase of the content of CaZrO\textsubscript{3}, CaO content is increased, so the generated CA\textsubscript{6} volume also increased significantly, leading to sample, loose structure, expansion, resulting in wear resistance is decreased obviously. From the point of abrasion resistance index of the sample, CaZrO\textsubscript{3} addition amount of 2\%~4\%.

3.4 Influence of CaZrO\textsubscript{3} on castables' slag resistance

A) 0\% (permeation depth 4.0 mm)  B) 2\% (permeation depth 1.0 mm)
C) 4\% (permeation depth 1.5 mm)  D) 6\% (permeation depth 3.0 mm)
E) 8% (permeation depth 3.5mm)  F) 10% (permeation depth 4.5mm)

**Figure 4.** Effect of MZ content on castables' slag resistance

It can be seen clearly from the figure 4, when adding 2%CaZrO$_3$, its best slag resistance, erosion depth of only 1.0 mm, the main reason has two: (1) Small amount of CaO and Al$_2$O$_3$ reaction to generate CA$_6$ in matrix, the microstructure of the material was optimized, so as to improve the slag resistance of sample;(2) ZrO$_2$ and CaO itself high temperature resistance, chemical stability, good resistance to alkali slag erosion performance[5]. However, can be seen from the figure 4, when the amount of CaZrO$_3$ from 6% to 10% range, with the improvement of CaZrO$_3$ content, sample volume expansion, internal structure is loose, porosity, bulk density is reduced, resulting in resistance to slag erosion resistance showed a trend of decrease. But in general, when adding 2%CaZrO$_3$, the sample has good resistance to slag erosion resistance.

4. Conclusions

(1) Adding 2%~4% CaZrO$_3$ can improve the strength of castables and wear resistance performance;

(2) With the increase of the content of CaZrO$_3$ sample volume density is declined slightly, apparent porosity is increased, the permanent linear rate is increased obviously;

(3) With the addition of more CaZrO$_3$, slag corrosion resistance of castables is declined;

(4) From the perspective of the comprehensive performance of castable, fused CaZrO$_3$ suitable addition amount is 2 ~ 4%.

References

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