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Influence of fused zirconium corundum addition on properties of chrome-free castables for RH refining furnace

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Abstract

Based on the operation conditions of RH refining furnace, this paper investigates the influence of fused zirconium corundum (for short ZA or FZA) additive on the performance of corundum–spinel castables, such as the cold modulus of rupture (CMOR), cold crushing strength (CCS), permanent linear change, thermal shock resistance and slag resistance. Corundum and spinel were the main raw materials of the samples with addition of proper amounts of micro powders and high effective dispersant. The samples, after dried at 110 °C for 24 h, then were fired at 1000 °C, 1400 °C and 1550 °C for 3 h, respectively. The monitoring results showed that ZA addition could greatly improve the CMOR, CCS, thermal shock resistance and slag resistance of castables simultaneously.

Keywords: C. Thermal shock resistance; RH refining furnace; Chrome-free castables; Fused zirconium corundum; Slag resistance

1. Introduction

Among many kinds of out-of-furnace refining process technologies, the RH vacuum degassing method is greatly admissive due to its good degassing efficiency, low reduction of molten steel temperature, as well as flexible and reliable operation conditions [1]. By now, direct bonded or rebonded magnesite chrome bricks have been widely used in the liner of RH refining furnace because they can survive the harsh conditions of refining environment. However, one of the problems for using such bricks is that they will produce poisonous hexavalent chromium at high temperatures, which causes great damage to the environment. Corundum–spinel castables are regarded as one of the best substitutes for magnesite chrome bricks in this area owing to their excellent properties, such as high strength, good abrasion resistance, high-temperature volume stability, good thermal shock resistance and high basic slag resistance [2]. Nevertheless, with the development of more effective productivity of RH, this kind of refractories often suffer from more severer conditions, for instance, high temperature fluctuations and high basic slag (R≥2.5) erosion, so it is importance to improve their properties, for basic slag resistance. Therefore, based on corundum–spinel system, in order to further improve the service life of chrome-free refractories in RH refining furnace, this paper investigates the influence of different amounts of fused zirconium corundum addition on the strength, thermal shock resistance and high basic slag corrosion resistance. which probably further improves the service life of chrome-free refractories in RH refining furnace.

2. Experimental procedures

2.1. Raw materials and preparation method

Dense corundum (5–3 mm), fused white corundum (3–1 mm, 1–0 mm, ≤0.074 mm), aluminum rich fused spinel (≤0.045 mm), CA-80 cement and active α-Al_2O_3 powder were used as the raw materials and the details of these are provided in Table 1. In order

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to investigate the influence of ZA, refractories were formulated by varying ZA (1–0 mm) content between 0 and 10 wt% to partially replace fused white corundum in the castables, as mentioned in Table 2. Firstly, All the raw materials were weighted according to the compositions and mixed for 1–2 min. Then reasonable amount of water was added and mixed for another 2–3 min to obtain the proper flowability. After that, the mixtures were casted into samples with the dimension of 160 mm × 40 mm × 40 mm. The samples were demoulded after curing in room temperature for 24 h, and then dried at 110 °C for another 24 h. Finally, the samples were sintered in the electric furnace from room temperature to 1000 °C, 1400 °C and 1550 °C and tempered at the final temperatures for 3 h, respectively.

2.2. Tests and characterization methods

The apparent porosity and bulk density of the samples were measured by the Archimedes drainage method according to GB/T 2997-2000. As well, the cold modulus of rupture (CMOR) was obtained by three-point bending test according to the GB/T 3001-2000, meanwhile, the cold crushing strength (CCS) was measured according to the GB/T 3997. 2-1998. The permanent linear change rate and thermal shock resistance of the samples were tested according to GB/T 5203-1993 and YB/T2206.2-1998, respectively. The slag resistance test of the samples was carried out by putting certain amount of refining ladles slag (shown in Table 3) into crucible and sintering at 1600 °C for 3 h. The microstructure and micro-area compositions of the samples were checked by scanning electron microscopy (SEM, Quanta 400, FEI Company, Holland) equipped with energy dispersive X-ray spectroscopy (EDS, Noran 623M-3SUT, Thermo Electron Corporation, Japan).

3. Results and discussion

3.1. Room temperature strength

Fig. 1 shows the CMOR and CCS of the castables with different amounts of ZA after sintered at different temperatures. Obviously, with the increase of ZA amount, the CMOR and CCS of castables didn't change much after treated at 110 °C, 1000 °C and 1400 °C, however, decreased a little after the castables treated at 1550 °C. At 110 °C, the strength of the castables was mainly attributed to the cement hydration products, such as CA and CA_2, as well as the loss of free water and some bonding water [2]. Therefore, the strength of samples varied little with different amounts of ZA. When the temperature raised to 1000 °C, the strength decreased a little due to the decomposition of all the hydration products as well as phase transformation of alumina. When the castables were treated at 1400 °C and 1550 °C, CaO reacted with Al_2O_3 to generate CA_6 in the matrix, leading to the enhancement of the strength. However, with the increase of ZA amount, the strength of castables after treated at 1550 °C decreased dramatically comparing with that at 1400 °C, which was due to the decline of bonding strength between aggregates and matrix together with addition of ZA. The strength of castables sintered at 1400 °C and 1550 °C were similar because the formation of CA_6 at these two temperatures were almost completed.

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

Material	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	ZrO_2
Dense corundum	98.31	0.21	0.03	0.02	0.15	–
Fuse white corundum	99.51	0.22	0.03	0.02	0.30	–
Fused spinel	77.56	–	–	20.35	–	–
Al_2O_3 power	98.90	0.23	–	–	0.08	–
CA-80 cement	77.89	–	19.12	–	–	
ZA	72.14	0.53	–	–	0.12	25.91

Table 2
Compositions of the corundum–spinel castables (wt%).

Raw material	1#	2#	3#	4#	5#	6#
Fused corundum (5–0 mm)	76	74	72	70	68	66
Fused spinel (325BS~1 mm)	10	10	10	10	10	10
Active alumina	10	10	10	10	10	10
CA-80 cement	4	4	4	4	4	4
ZA (1–0 mm)	0	2	4	6	8	10
Dispersant	adequate	adequate	adequate	Suitable		

Table 3
The compositions of slag used for slag resistance (wt%).

Composition	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2	MFe	P	S
Content (wt%)	10.40	23.69	5.46	4.69	34.64	14.60	0.36	1.36	0.13	0.029

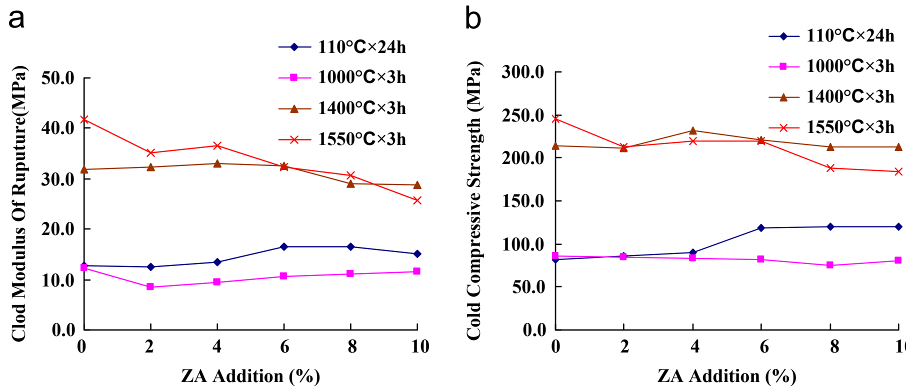

Fig. 1. CMOR and CCS of castables containing different amounts of ZA after fired at various temperatures. (a) CMOR and (b) CCS.

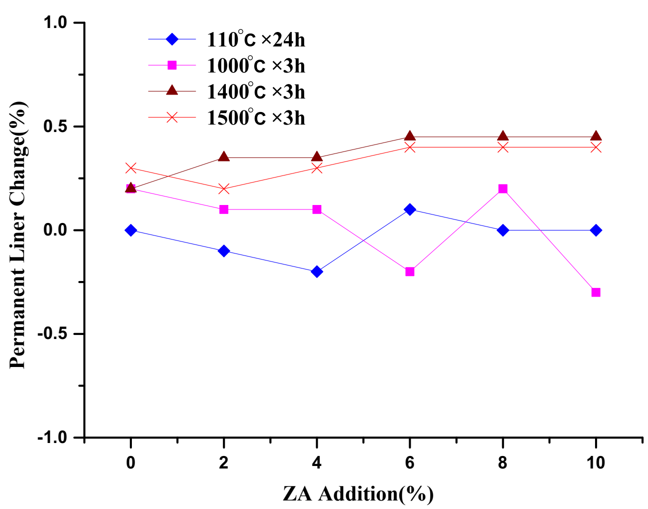

Fig. 2. Permanent linear change of castables containing different amounts of ZA after fired at various temperatures.

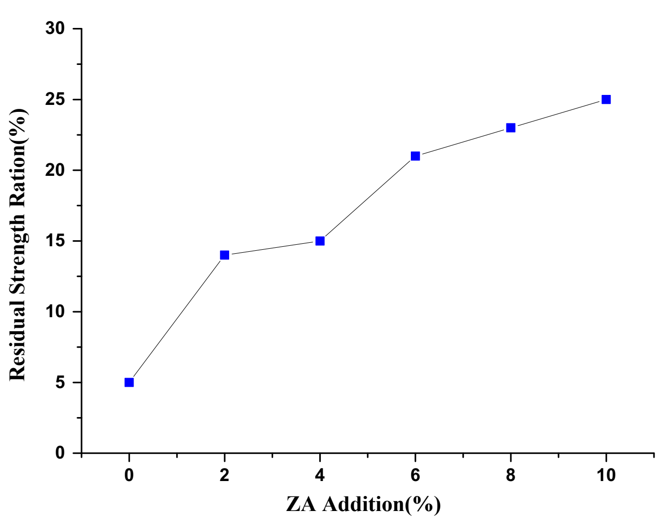

Fig. 3. The residual strength conservation as a function of ZA addition.

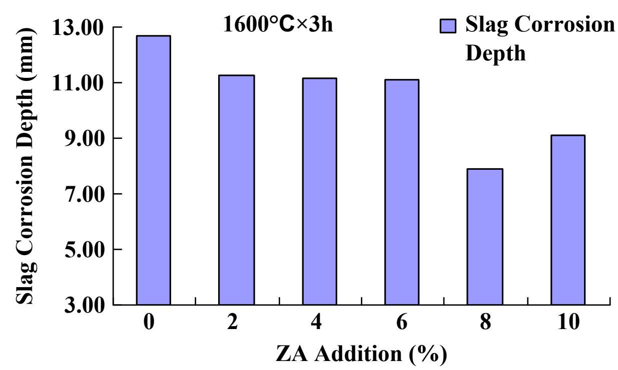

Fig. 4. The slag erosion depth as a function of the amount of ZA addition.

3.2. Permanent linear change

Fig. 2 shows the influence of ZA amounts on the permanent linear change of castables after treated at different temperatures. Obviously, with the increase of treated temperature, the permanent linear change of castables was gradually transformed from "shrinkage" to "expansion", especially for the samples treated at 1400 °C and 1500 °C which contributed to the formation of large amount of CA_6. With the increasing addition of ZA, was attributed to the transformation of ZrO_2 phase from tetragonal structure to monoclinal structure. Moreover, it is obvious that the permanent linear change varied in a small range when the amount of ZA changed, which was favorable for high temperature volume stability and avoidance of cracks formations. The permanent linear rate of samples containing different amounts of ZA after sintered at different temperatures was similar and changed in the range from 0 to 0.5%.

3.3. Thermal shock stability

Fig. 3 shows the influence of ZA amounts on the thermal shock resistance of castables after treated at different temperatures. It is obvious that residual strength conservation of castables was improved that with the increase of the amount of ZA addition after three thermal shock cycles (1100 °C, water cooled), while it still remained 25% for the samples containing 10 wt% ZA after thermal shock test, attributed to the transformation of ZrO_2 phase and microcrack toughening effect. In the condition of high temperature, these microcracks can effectively absorb the thermal stress, therefore, the thermal shock resistance of castables was obviously improved [3].

3.4. Slag resistance

Fig. 4 shows the slag corrosion depth in the castables as a function of the amount of ZA addition after slag test. With the increase of ZA amount from 0 to 8 wt%, the slag corrosion depth decreased accordingly, which indicating that the slag resistance improved greatly. On one hand, fused zirconium corundum has high density, high strength, and good corrosion resistance. On the other hand, the zirconium can not react with slag at high temperature, therefore, the slag resistance of castables was improved effectively.

4. Conclusions

(1) The residual strength conservation of castables with the increase of the amount of ZA addition, while it still remained 25% for the samples containing 10 wt% ZA after thermal shock test.
(2) The permanent linear rate of samples containing different amounts of ZA after sintered at different temperatures was similar and changed in the range from 0 to 0.5%.
(3) Compared with samples without ZA, the addition of ZA greatly improved the slag resistance of castables, especially for the samples which contained 8 wt% of ZA decreased the corrosion by about 38%.

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