

Improvement in performance of MgO–CaO refractories by addition of nano-sized ZrO₂

Min Chen*, Caiyun Lu, Jingkun Yu

School of Materials and Metallurgy, 312# Northeastern University, 3-11 Wen-Hua Road, Shenyang 110004, China

Received 21 December 2006; received in revised form 28 February 2007; accepted 14 April 2007

Available online 11 June 2007

Abstract

MgO–CaO refractories added with different sized ZrO₂ powders were sintered at 1600 °C, the effect of the ZrO₂ powders on performance of MgO–CaO refractories was investigated. The results showed that the densification of the MgO–CaO refractories was appreciably promoted when a small amount of ZrO₂ was added owing to the formation of small size CaZrO₃ facilitated to sintering, and the densification was promoted further with increasing the amount of ZrO₂ due to the volume expansion caused by the reaction of the added ZrO₂ and CaO to form CaZrO₃ in the refractories, and the addition of nano-sized ZrO₂ was more effective. The thermal shock resistance of the MgO–CaO refractories was improved by modification of the microstructure due to the formed CaZrO₃ particles that predominately located on the grain boundaries and triple points in the whole microstructure, and the addition of nano-sized ZrO₂ was more effective attributed to its well dispersion and the critical addition amount was effectively decreased to 6%. The slaking resistance of the MgO–CaO refractories was appreciably improved by addition of ZrO₂ due to its effect on decreasing the amount of free CaO in the refractories, promotion of densification as well as modification of microstructure, the nano-sized ZrO₂ addition was more effective due to its higher activity. The slag corrosion resistance of the MgO–CaO refractories was enhanced by addition of ZrO₂ due to the increase of the viscosity of the liquid phase and thus inhibited further penetration of slag at elevated temperatures.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Refractories; MgO–CaO–ZrO₂; Sintering; Thermal shock resistance; Corrosion

1. Introduction

MgO–Cr₂O₃ refractories have been widely used in VOD furnace and cement rotary kilns for their excellent properties such as high refractoriness, excellent slag corrosion resistance and thermal shock resistance.¹ Whereas, toxic hexavalent chromates, which were formed easily in the presence of alkalis oxidizing atmosphere, would degenerate the chrome-ore of MgO–Cr₂O₃ refractories and caused environment problems. Recently, an increase in environmental concerns has been attracting people to pay much attention on this subject and many studies had been carried out to develop new type environment friendship refractories to substitute MgO–Cr₂O₃ refractories.^{2–4}

MgO–CaO refractories are considered to be one type of chrome-free refractories to substitute MgO–Cr₂O₃ refractories for their properties of excellent stability at high temperatures and corrosion resistance to alkalinity slag.^{5,6} In addition, MgO–CaO

refractories have the advantage to remove inclusions from molten steel and favorite to clean steel product,^{7,8} and thus MgO–CaO refractories have been considered to be one type of potential refractories for clean steel product.⁹ However, the application of MgO–CaO refractories has been inhibited for their poor thermal shock resistance and hydration resistance. It has been reported that the addition of ZrO₂ can appreciably improve the properties of the MgO–CaO refractories, but it causes the price of product appreciably rising. Therefore, it is important to decrease the amount of ZrO₂ for the purpose to improve the properties of the MgO–CaO refractories.

Nano-technology has been introduced to refractories in recent years. It has been reported that the performance of the refractories was appreciably improved for the well dispersion of nano-sized particles in the microstructure and reaction activity.^{10–14} Therefore, the present work investigated the effect of nano-sized ZrO₂ addition on sintering and properties of the MgO–CaO refractories by comparing with micro-sized ZrO₂ addition. The purpose of the work is to study the effect of nano-sized ZrO₂ addition on the properties of MgO–CaO refractories

* Corresponding author. Tel.: +86 24 6368 2241; fax: +86 24 8368 1576.
E-mail address: slakejp@163.com (M. Chen).

Table 1
Chemical composition of as-received MgO–CaO clinker and cement clinker

Materials	MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
As-received MgO–CaO clinker	72.59	23.50	1.26	1.52	0.48
Clinker of cement	4.67	52.80	26.34	7.41	2.31

so as to confirm the possibility to improve the properties of the refractories with less ZrO₂ addition by nano-technology.

2. Experimental procedures

The starting material was as-received MgO–CaO clinker, with chemical composition as shown in Table 1. Two kinds of high-purity ZrO₂ powders with properties as shown in Table 2 were used as additives.

The two kinds of ZrO₂ powders with mass percent of 0–8% were dry-mixed with the as-received MgO–CaO clinker that was sieved to pass 150 mesh, respectively. Then the mixed powders were one-axial shaped to pellet samples sized $D20\text{ mm} \times 6\text{ mm}$ under a pressure of 200 MPa. The samples were heated in an electric furnace at a rate of 5 °C/min to 1600 °C and kept for 3 h, and then cooled to room temperature in furnace.

The sintered samples were characterized by carrying out bulk density and apparent porosity, phase compositions, microstructure analyses, thermal shock resistance, slaking resistance as well as slag corrosion resistance. The bulk density and apparent porosity were measured by immersion method in kerosene under vacuum using Archimedes' principle and calculated according to the following equations¹⁵:

$$\text{bulk density (g/cm}^3\text{)} = \frac{m_1 d}{m_3 - m_2} \quad (1)$$

$$\text{apparent porosity} = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \quad (2)$$

where m_1 is the mass of a dried sample in air (g), m_2 the mass of the sample in kerosene (g), m_3 the mass of the sample with free bubbles on the surface (g), and d is the density of kerosene (g/cm³).

Phase compositions were analyzed by X-ray powder diffraction (XRD, Cu target, 30 kV and 30 mA). The microstructure was observed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyzer (EDX) on the fractured surfaces after thermal etching at 1400 °C for 30 min. The thermal shock resistance was evaluated by quenching the samples in air for 15 min after heating at 1100 °C for 15 min, and this test was recycled till the sample ruptured. The slaking resistance of the samples was evaluated by measuring the mass gain after soaking under the conditions of 60 °C and 70% relative

Table 2
Properties of the high-purity ZrO₂ powders

ZrO ₂ powder	Purity (mass%)	Average size
Micro-sized	99.5	30 μm
Nano-sized	99.9	46 nm

humidity for 96 h. The slag corrosion test was carried out according to the following processing route: first, the hand-pressed pieces sized $D8\text{ mm} \times 5\text{ mm}$ of cement clinker (composition as shown in Table 1) were deposited on surfaces of samples, then the couples clinker-substrate were treated at a rate of 5 °C/min to 1500 °C and kept for 3 h. The slag corrosion resistance was evaluated by comparing the degree of penetration and erosion.

3. Results and discussion

3.1. Densification

Fig. 1 shows the effect of ZrO₂ addition on bulk density and apparent porosity of the sintered samples. It is observed that the bulk density increased appreciably with 2% ZrO₂ addition and then increased slightly with further increasing ZrO₂ from 2% to 8%. At the same time, the apparent porosity decreased appreciably with a small amount of ZrO₂ addition and decreased slightly with further increasing ZrO₂ addition. It is also observed that the bulk density of the sample with nano-sized ZrO₂ addition was higher than that with micro-sized one. From these results, it is known that the addition of ZrO₂ promoted the densification of MgO–CaO refractories and nano-sized ZrO₂ addition was more effective.

3.2. Phase composition and microstructure

Fig. 2 shows the XRD patterns of samples without addition, with 2% and 4% nano-sized ZrO₂. In the sample without addition, MgO and CaO were the main crystalline phases. Simultaneously, in the sample with 2% and 4% nano-sized ZrO₂, MgO, CaO and CaZrO₃ were the main crystalline phases, and no ZrO₂ phase coexisted, furthermore, the intermediate compounds CaZr₄O₉, Ca₆Zr₁₉O₄₄, Mg₂Zr₅O₁₂, and MgZr₆O₁₃,^{16–18} which have been generally admitted in CaO–ZrO₂ and MgO–ZrO₂ subsystems, were not detected. It indicates that all added ZrO₂ had reacted with CaO to form the only resultant, CaZrO₃. No change in lattice parameter of MgO phase was measured when ZrO₂ was added indicates that ZrO₂ did not formed solid solution with MgO.

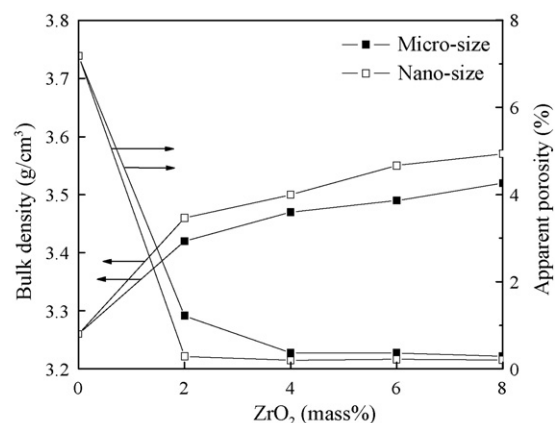


Fig. 1. Effect of ZrO₂ addition on densification of the MgO–CaO refractories.

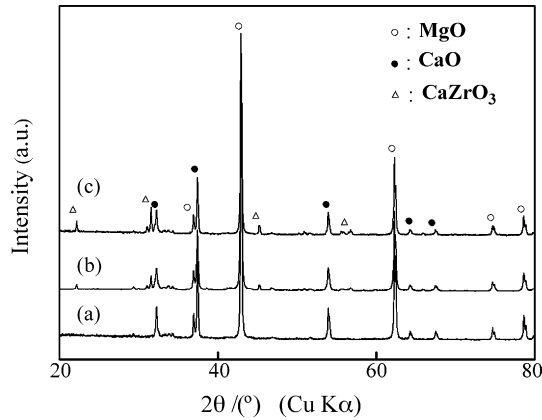


Fig. 2. XRD patterns of MgO–CaO refractories: (a) without addition, (b) with 2% and (c) with 4% nano-sized ZrO₂ addition.

Therefore, it is considered that the densification of MgO–CaO refractories was promoted by addition of ZrO₂ in the following two aspects:

- (1) The formation of CaZrO₃ by adding a small amount of ZrO₂ enhanced the sintering of the MgO–CaO refractories and thus the densification was promoted. Since nano-sized ZrO₂ has significant surface effects, size effects, and quantum effects, it would react with CaO at lower temperature and formed smaller size CaZrO₃, which preferred to locate on intragranular and intergranular sites of MgO and CaO grains and prone to cause crystal lattice defects. As a result, the addition of nano-sized ZrO₂ was more effective on densification than the micro-sized one.
- (2) With further increasing the addition of ZrO₂, the 7–8% volume expansion caused by the formation of CaZrO₃ contributed to decreasing the pore size between the oxides grains, and thus the densification was promoted. In addition, the increase of real density^{19,20} with increasing the amount of ZrO₂ also facilitated to increase the bulk density of the MgO–CaO refractories.

Fig. 3 shows the typical microstructure of the fractured surfaces of samples with various amount of nano-sized ZrO₂. For the sample without addition, due to the impurities in the starting materials, some low melting point phases were observed at grain boundaries and triple points besides MgO (dark gray) and CaO (light gray) grains (Fig. 3a). EDX analyses indicate that these low melting point phases were formed by the reaction of CaO with impurities of Al₂O₃, Fe₂O₃ and SiO₂ to generate calcium aluminates, calcium silicate, calcium ferrite, calcium ferritealuminate, etc. When ZrO₂ was added, it reacted with a part of CaO to form CaZrO₃, MgO (dark gray), CaO (light gray), and CaZrO₃ (white) were observed in the microstructure (Fig. 3b–d), EDX analyses indicate that a small quantity of ZrO₂ was observed in the low melting point phases.

It is considered that the addition of ZrO₂ influences the densification of the MgO–CaO refractories in two aspects: on one side, the addition of ZrO₂ promoted densification due to the formation of small size CaZrO₃ particles with crystal defects and high activity, on the other side, the formed CaZrO₃ as a second phase inhibited grain growth and densification of the MgO–CaO refractories. The two aspects caused the results as follow: when a small amount of ZrO₂ was added, the former was the determinant factor, the densification of the MgO–CaO refractories was promoted and the grains grew up (Fig. 3b). With increasing the amount of ZrO₂, the later was the determinant factor, and the grain size was slightly decreased (Fig. 3c and d). In addition, since a part of CaO was consumed to form CaZrO₃, the chance of CaO to react with impurities was decreased and thus the formed amount of low melting point phases decreased.

3.3. Improvement on properties

Fig. 4 shows the relationship between thermal shock resistance and the amount of ZrO₂. It is observed that the thermal shock resistance was improved by addition of ZrO₂, and the addition of nano-sized ZrO₂ was more effective. The thermal shock times of the sample with 4% nano-sized ZrO₂ addition was correspondent to the one with 6% micro-sized addition. And the effect of 6% nano-sized ZrO₂ addition was better than

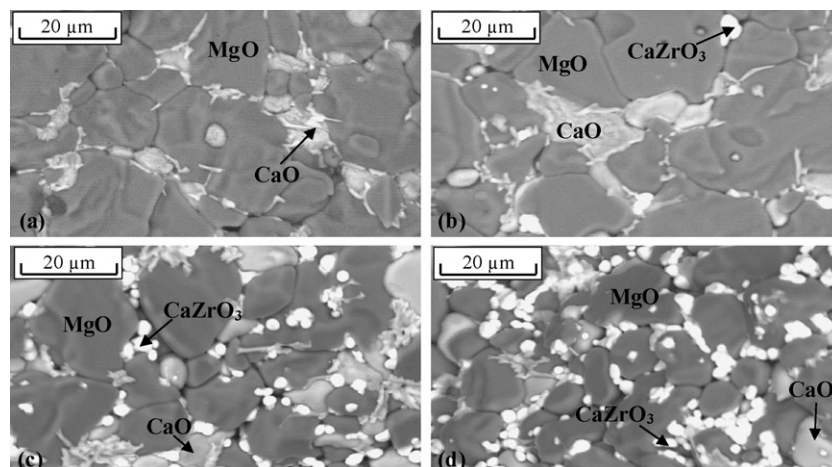


Fig. 3. SEM images of fractured surfaces of the samples with various nano-sized ZrO₂ addition: (a) without ZrO₂, (b) 2% ZrO₂, (c) 4% ZrO₂ and (d) 8% ZrO₂.

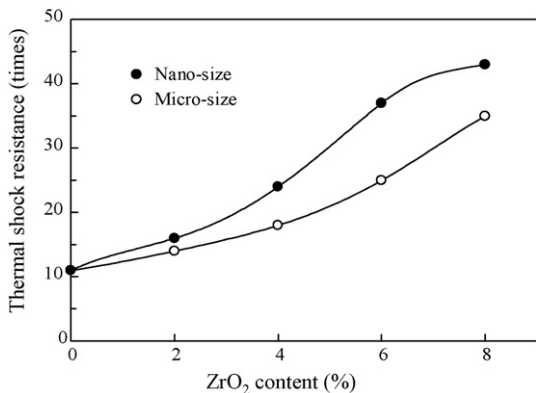


Fig. 4. Improvement in thermal shock resistance of MgO–CaO refractories by addition of ZrO₂.

that of 8% micro-sized one. Due to the different thermal expansion coefficients between CaO ($13.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$),²⁰ MgO ($13.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$)²¹ and the formed CaZrO₃ ($7.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ from 20 to 1000 °C),²² microcracks would prefer to generate between CaZrO₃ and MgO or CaO during thermal shock process. It is considered that the formation of these microcracks would effectively slow down and/or interrupted microcrack propagation and thus the thermal shock resistance was improved. Owing to well dispersion and homogeneous microstructure formed, the nano-sized ZrO₂ addition was more effective than the micro-sized one.

It is also observed from this figure that the curve with nano-sized ZrO₂ addition tends to reach a constant when the amount of nano-sized ZrO₂ addition was more than 6%. But for the micro-sized one, the thermal shock times was still increasing even though 8% was added. Therefore, it is considered that for the purpose to improve thermal shock resistance of MgO–CaO refractories, the critical amount of nano-sized ZrO₂ addition was about 6%, but it was more than 8% for micro-sized one. Thus, it could be concluded that the addition of nano-sized ZrO₂ could effectively decrease the necessary amount of ZrO₂ for improving the thermal shock resistance of MgO–CaO refractories.

Fig. 5 shows the effect of ZrO₂ addition on slaking resistance of MgO–CaO refractories. It is observed that the mass gain of the

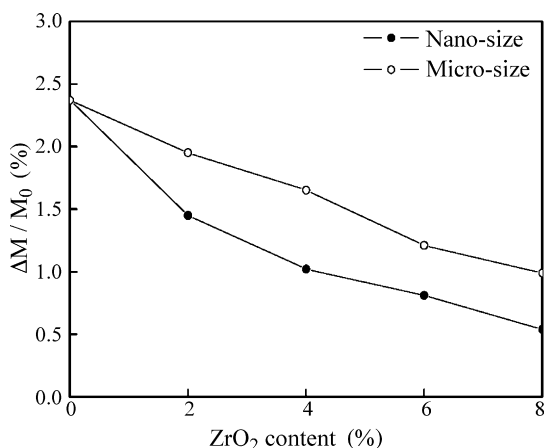


Fig. 5. Effect of ZrO₂ addition on improvement of slaking resistance.

MgO–CaO refractories decreased appreciably with ZrO₂ addition. For the sample without addition, the mass gain after 96 h was 2.37%, which was sharply decreased with increasing the amount of ZrO₂. The mass gain was decreased to 1.95% when 2% micro-sized ZrO₂ was added, and it was merely 1.45% when the same amount of nano-sized ZrO₂ was added, indicating that the improvement of hydration resistance by nano-sized ZrO₂ addition was about twice as micro-sized ZrO₂ addition. With further increasing the amount of ZrO₂ addition, the mass gain decreased further.

It is known that the slaking resistance of CaO containing materials, both rich-CaO (details as described in a previous paper²³) and rich-MgO materials, is strongly dependent on the content of free CaO in the materials and its microstructure.^{24–26} When ZrO₂ was added, the promotion on slaking resistance of the refractories is considered due to the following reasons.

First, the slaking resistance of MgO–CaO refractories was improved by converting part of free CaO to unhydrated CaZrO₃ and surrounding another part of free CaO in MgO and CaZrO₃ particles. With increasing the addition of ZrO₂, the content of free CaO in the refractories decreased further and thus the slaking resistance of the refractories was improved.

Second, the promotion of densification by addition of ZrO₂ decreased the porosity of the refractories and thus its reaction specific area was decreased while the refractories were exposed to humidity environment.

Third, the slaking resistance of the refractories was improved by modification of the microstructure. It is well-known that the slaking reaction always begins from the sites with crystal defects. Thus, the grain boundaries, especially the triple points, are the poor slaking resistant sites. When ZrO₂ was added, the formed CaZrO₃ predominately located at grains boundaries and triple points of CaO and MgO grains. Thus, the slaking resistance of the refractories was appreciably improved by addition of ZrO₂. As well dispersing of the formed CaZrO₃ and preference on occupying these poor slaking resistant sites, the addition of nano-sized ZrO₂ was more effective on improvement of slaking resistance.

Figs. 6 and 7 show the polished cross-sections of the refractories after slag corrosion test. In both figures, Figs. 6b and 7b are the magnified photos of the erosion zone as circled in Figs. 6a and 7a. It is observed that the hand-pressed clinkers substantially adhered to the substrate surface in both samples though the interface was still observed, and a reaction zone (erosion zone, shown in Figs. 6b and 7b) was formed. It is also observed that the penetration depth (D_p) of the sample with nano-sized ZrO₂ addition was much decreased than that of the sample without addition though the erosion depth (D_E) of the former was slightly increased. Under the erosion zone, some liquid penetrated through grain boundaries and pores. And under the penetration zone, substrates remain as their original microstructure. These results are considered to be due to the follows two aspects.

On one hand, as fine CaZrO₃ grains dispersed on the boundaries and triple points of MgO and CaO grains and the content of low melting point phases was decreased, thus the growth of MgO and CaO grains was inhibited and the grain size of

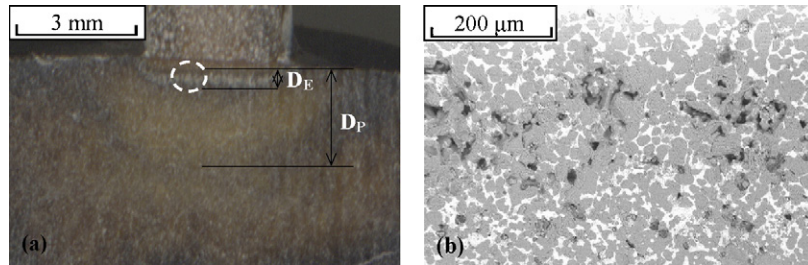


Fig. 6. Polished cross-sections by (a) optical microscopy and (b) SEM of the sample clinker-substrate without ZrO_2 .

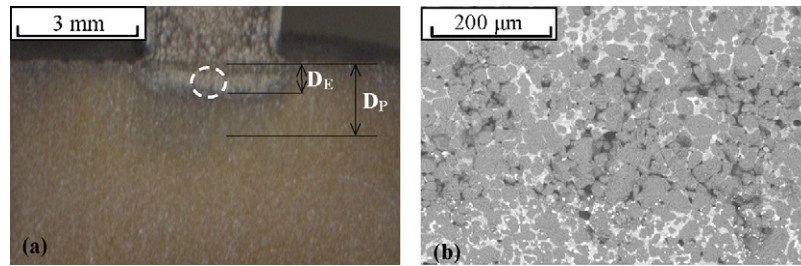


Fig. 7. Polished cross-sections by (a) optical microscopy and (b) SEM of the sample clinker-substrate with 4% nano-sized ZrO_2 .

them was decreased. Consequently, the dissolution of MgO , especially CaO , into slag was enhanced. As a result, the erosion of the sample with 4% nano-sized ZrO_2 was observed slightly severe compared to that one without addition. But, owing to the adherence ability of cement clinker on refractories was influenced by the chemical reaction between cement clinker and refractories,^{27,28} the sample with 4% nano-sized ZrO_2 is considered favorable to form slag coatings on the surface of the refractories compared to the sample without ZrO_2 , which contributes to improve the slag corrosion resistance of the refractories.

On the other hand, it is considered that the increasing in viscosity of low melting point phases by introducing $CaZrO_3$ ²⁹ that formed by the reaction of the added ZrO_2 and CaO not only inhibits the low melting point phases penetrating into substrate, but also consider contributing to forming self-protective coatings on the surface of the refractories.

Table 3 shows the slag corrosion test results of the MgO – CaO refractories without addition, with 4% micro-sized and 4% nano-sized ZrO_2 addition, respectively. It is observed that the penetration index of the MgO – CaO refractories without addition was higher than that one with 4% micro-sized ZrO_2 addition, and the penetration index of the MgO – CaO refractories with 4% nano-sized ZrO_2 was least. Nevertheless, the erosion index

was reversed. It is known that the grains of the MgO – CaO refractories with ZrO_2 addition was inhibited to grow up, furthermore, the addition of nano-sized ZrO_2 was more effective on inhibition. As a result, the smaller grains were prone to dissolve into liquid phase, and caused more severe erosion. Meanwhile, the dissolving process caused the enrichment of ZrO_2 and improvement of viscosity of the liquid phase, consequently, the low melting point phase was inhibited to penetrate further.

4. Conclusions

The present work studied the effect of ZrO_2 addition on sintering and properties of MgO – CaO refractories. Based on the results above, it could be concluded as following:

- (1) $CaZrO_3$ was the only ternary compound in MgO – CaO – ZrO_2 system.
- (2) The densification of the MgO – CaO refractories was promoted by adding a small amount of ZrO_2 due to the formation of small size $CaZrO_3$ facilitated to sintering. Further promotion of densification with increasing ZrO_2 addition was contributed to the volume expansion caused by the reaction of the added ZrO_2 with CaO in the MgO – CaO refractories. The addition of nano-sized ZrO_2 was more effective since the smaller addition was more reactive.
- (3) The thermal shock resistance of the MgO – CaO refractories was improved by modification of microstructure by addition of ZrO_2 , and the addition of nano-sized one effectively decreased the critical added amount for improvement of thermal shock resistance.
- (4) The slaking resistance of the MgO – CaO refractories was appreciably improved by addition of ZrO_2 due to its effect on decreasing the content of free CaO in the refractories, promotion of densification as well as modification of

Table 3

Slag corrosion results of the MgO – CaO refractories without addition, with 4% micro-sized and with 4% nano-sized ZrO_2 addition

Terms	Erosion index	Penetration index ^a
Without addition	20	100
With micro-sized ZrO_2	22	84
With nano-sized ZrO_2	24	76

^a Note: The penetration index of MgO – CaO refractories without ZrO_2 is regarded as 100, the others are percentages compared to it.

microstructure. The nano-sized ZrO_2 addition was more effective owing to its higher activity.

- (5) The slag corrosion resistance of the MgO–CaO refractories was improved by addition of ZrO_2 which effectively prevented slag penetrating into the MgO–CaO refractories and would contribute to form the self-protective coatings on the surface of the refractories. The nano-sized ZrO_2 addition was more effective due to its intrinsic properties.
- (6) For the purpose to improve the properties of the MgO–CaO refractories, the addition of ZrO_2 could be effectively decreased by nano-technology.

References

1. Lee, W. E. and Moore, R. E., Evolution of in-situ refractories in the 20th century. *J. Am. Ceram. Soc.*, 1998, **81**, 1385–1410.
2. Guo, Z. Q., Palco, S. and Rigaud, M., Bonding of cement clinker onto Doloma-based refractories. *J. Am. Ceram. Soc.*, 2005, **88**, 1481–1487.
3. Bray, D. J., Toxicity of chromium compounds formed in refractories. *Ceram. Bull.*, 1985, **64**, 1012–1016.
4. Driscoll, M. O., Price temper steel market promise. *Ind. Miner.*, 1994, **324**, 35–49.
5. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. Wiley-Interscience, New York, 1975, p. 547.
6. Zhu, X., Sun, Q. and Liao, C., Effects of zircon on the structure and properties of MgO–CaO system material (in Chin.). *Refractories/Naihuo Cailiao (Eng. Transl.)*, 1995, **29**(6), 320–323.
7. Feng, W. X., Niu, J. G., He, H. M., Su, S. H., Liu, Y., Chen, L. Y. and Liu, H. K., Influence of MgO–CaO based spraying material and CaO based cover flux for tundish on steel cleanness. *Kang T'ieh/Iron and Steel (China)*, 2002, **37**, 25–27.
8. Wei, Y. W. and Li, N., Refractories for clean steel making. *Am Ceram. Soc Bull.*, 2002, **81**, 32–35.
9. Zhong, X. C., Looking ahead—a new generation of high performance refractory ceramics. *Refractories/Naihuo Cailiao (China)*, 2003, **37**, 1–10.
10. Preface for JAIST International Symposium on Nano Technology 2005. *Sci. Technol. Adv. Mater.*, 2006, 7229–7230.
11. Gleiter, H., Nanocrystalline materials: basic concept and microstructure. *Acta Mater.*, 2000, **48**, 1–29.
12. Tjong, S. and Chen, H., Nanocrystalline materials and coatings. *Mater. Sci. Eng. Res.*, 2004, **45**, 1–88.
13. Johnston, K. and Shah, P., Making nanoscale materials with supercritical fluids. *Science*, 2004, **303**, 482–483.
14. Ferkel, H. and Hellmig, R. J., Effect of nanopowders deagglomeration on the densities of nanocrystalline ceramic green body and their sintering behavior. *Nanostruct. Mater.*, 1999, **11**, 617–622.
15. JIS R2205, 1992.
16. Serena, S., Sainz, M. A., De Aza, S. and Caballero, A., Thermodynamic assessment of the system ZrO_2 –CaO–MgO using new experimental results. Calculation of the isoplethal section MgO–CaO– ZrO_2 . *J. Eur. Ceram. Soc.*, 2004.
17. Delamarre, C., Existence and structure of a new compound of formula M_7O_{12} in zirconia–magnesia and hafnia–magnesia systems. *C.R. Hebd. Seances Acad. Sci. Ser. C*, 1965, **269**, 113–115.
18. Hannink, R. H. J. and Garvie, R. C., Subeutectoid aged Mg–PSZ alloy with enhanced thermal up-shock resistance. *J. Mater. Sci.*, 1982, **17**, 2637–2643.
19. Yukiteru, K. et al., Properties of fused zirconia refractory materials. *Taikabutsu Overseas*, 1997, **17**(2), 3–8.
20. Hu, B. Y., Xu, Y. Q. and Zhang, H. D., *Special Refractories Operative Technology Directory*. Metallurgical Industrial Press, China, 2004.
21. De Aza, S., Reaction sintering of zircon/dolomite mixtures. *J. Eur. Ceram. Soc.*, 2001, **21**, 343–354.
22. Richardson, D. W., *Modern Ceramic Engineering. Properties Processing and Use in Design*. Marcel Dekker, 1992.
23. Chen, M., Wang, N., Yu, J. and Yamaguchi, A., Preparation of slaking resistant CaO aggregate from lightweight $CaCO_3$ with oxide addition. *Mater. Lett.*, 2006.
24. Shirogawa, A., *Sintering and hydration properties of CaO containing composite*. MD Thesis. Nagoya Institute of Technology, Japan, 1996.
25. Cutler, I. B., Felix, R. L. and Caywood Jr, L. P., Increasing hydration resistance of calcia. *Am. Ceram. Soc. Bull.*, 1970, **49**, 531–533.
26. Oda, Y., Preventive methods for hydration of calcia and dolomite clinkers. *Taikabutsu (Japan)*, 1989, **41**, 690–700.
27. Hiragushi, K., Shikano, H. and Ohishi, M., Cement clinker ticking properties of basic bricks in cement kilns. *Taikabutsu Overseas*, 1989, **9**(4), 15–19.
28. Rigaud, M., Guo, Z. Q. and Palco, S., Coating formation on basic bricks for rotary cement kilns. In XXIX Congreso Alafar 2000. ALAFAR-Asociacion Latinoamericana de Fabricantes de Refractories, Pucón, Chile, 2000, pp. 209–222.
29. Serena, S., Sainz, M. A. and Caballero, A., Corrosion behavior of MgO/CaZrO₃ refractory matrix by clinker. *J. Eur. Ceram. Soc.*, 2004, **24**, 2399–2406.