Materials and Design 186 (2020) 108326

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Fabrication and analysis of lightweight magnesia based aggregates containing nano-sized intracrystalline pores

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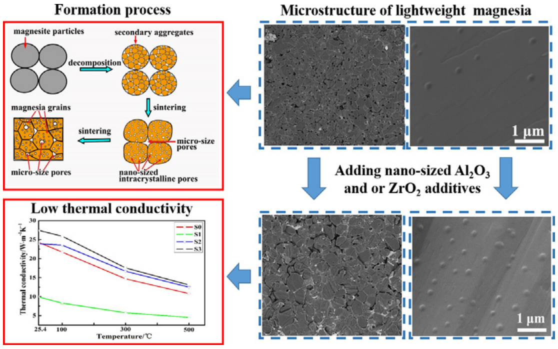
HIGHLIGHTS

- Lightweight magnesia aggregates with closed porosity of 4.3% and abundant nano-sized intracrystalline pores were prepared.
- Lightweight magnesia aggregates have lower thermal conductivity: 4.539 W·m^{-1}K^{-1} at 500 °C.
- 100~300 nm intracrystalline pores were formed by the sintering of small MgO crystallites inside pseudomorph of magnesite.
- Nano Al_2O_3 and ZrO_2 promoted the formation of intracrystalline pores by increasing their migration distance for separating.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 August 2019
Received in revised form 31 October 2019
Accepted 31 October 2019
Available online 08 November 2019

Keywords:
Lightweight refractories
Magnesia
Nano-sized intracrystalline pores
Sintering

ABSTRACT

To efficiently reduce heat loss in high-temperature furnaces, the use of a working lining with low thermal conductivity, in lightweight refractories is a significant development. Conventional lightweight refractories focus on the fabrication of Al_2O_3-based, spinel-based, or Al_2O_3-spinel based refractories with micro-sized closed pores. In this study, lightweight magnesia-based aggregates with smaller nano-sized pores were fabricated by the decomposition of magnesite by using nano-sized Al_2O_3 and ZrO_2 as additives. The lightweight magnesia containing nano-sized intracrystalline pores (100–300 nm) had a relatively low thermal conductivity of 4.539 W·m^{-1}K^{-1} at 500 °C with a bulk density of 3.37 g/cm^3 and a closed porosity of 4.3%. Moreover, the formation mechanism of nano-sized intracrystalline pores was proposed, and the effect of nano-sized additives on the sintering properties was discussed. We concluded that nano-sized Al_2O_3 and ZrO_2 raise the number of nano-sized intracrystalline pores by increasing their migration distance required to separate from the magnesia grains. With the joint addition of nano-sized Al_2O_3 and ZrO_2, the lightweight magnesia possessed the lowest thermal conductivity, as well as excellent strength, owing to the generation of intergranular $MgAl_2O_4$ spinel. Furthermore, the nano-sized Al_2O_3 and ZrO_2 also promoted the sintering of magnesia resulting in the formation of cation vacancies (V_{Mg}^{**}).

1. Introduction

Conventional refractories applied in high temperature industries are generally divided into three types: working lining refractories, permanent lining refractories, and insulating refractories according to their

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https://doi.org/10.1016/j.matdes.2019.108326

Table 1
Main chemical compositions of magnesite.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	IL
Mass fraction (wt%)	0.61	0.5	0.49	0.8	45.88	51.57

properties. Working lining refractories require high corrosion resistance since they involve direct contact with the molten liquid, and thus have high density. In comparison, insulating refractories are light and have many pores inside, resulting in low thermal conductivity [1]. The problem with working lining refractories is that they have poor heat-shielding performance, which results in a tremendous loss of energy. Simultaneously, the service life of insulating refractories is short, which is a waste of resources. With the ever increasing consumption of resources and energy globally, some researchers proposed the concept of using lightweight refractories in the working lining, with low thermal conductivity and high corrosion resistance [2]. Existing literature confirms that lightweight refractories have better heat-shielding performance because they are closer to the hot face [3–5]. Compared to conventional refractories, lightweight refractories combine the advantages of working lining refractories and insulating refractories, and have received much attention and development in recent years.

Designing lightweight aggregates is a key step in fabricating lightweight refractories. Lightweight aggregates are characterized by relatively low bulk density, low apparent porosity, high closed porosity, and smaller pore size. Many studies have been conducted to fabricate lightweight aggregates and investigate their performance. Fu et al. [6–9] fabricated lightweight micro-porous corundum aggregates using alumina micropowders as raw materials by adding nano-sized additives and a pore-forming agent. The nano-sized additives, due to their superplasticity, accelerated the migration of the grain boundary and significantly increased the closed porosity (12.3%), while decreasing the bulk density (3.05 g/cm^3) and apparent porosity (9.1%). They also exhibited good heat-shielding performance (3.73 W·m^{-1}K^{-1} at 800 °C, about 66.5% lower than dense corundum aggregates). Furthermore, they investigated the slag resistance, the results of which suggested that the micropores in aggregates lead to increased precipitation rates of second phases like $CaAl_{12}O_{19}$ (CA_6) and $CaAl_4O_7$ (CA_2) that form an isolation layer at the slag-aggregate interface and prevent further slag corrosion and penetration [4].

Yan et al. [3] prepared porous periclase-spinel ($MgAl_2O_4$) aggregates with an apparent porosity of 23.3% and a median pore size of 5.66 μm from magnesite and $Al(OH)_3$ by an in-situ decomposition pore-forming technique. When applied to castables, the porous aggregates exhibited strong bonding with the matrix and absorbed the penetrated slag to enhance their slag resistance. Similarly, Chen et al. [10] fabricated microporous corundum-spinel aggregates with an average pore size less than 10 μm by foam-gelcasting methods, the porosity and properties of which were strongly dependent on the content of the foaming agent. Their castables had a low thermal conductivity of 0.751 W·m^{-1}K^{-1} at 1000 °C, and high mechanical strength, but serious slag erosion occurred when the foaming agent content increased to 1.5 wt%.

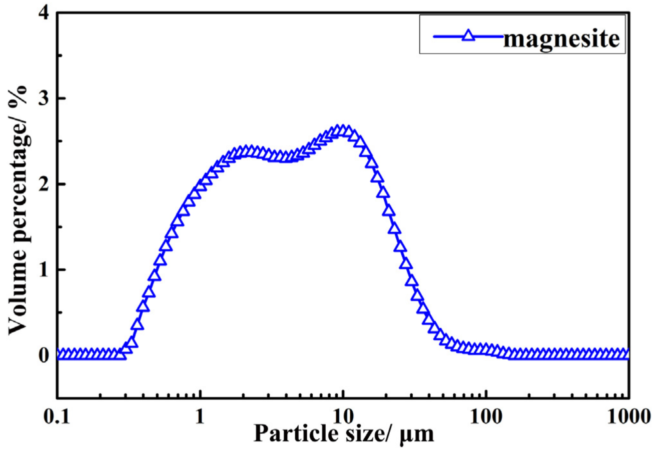

Fig. 1. Particle size distribution of magnesite.

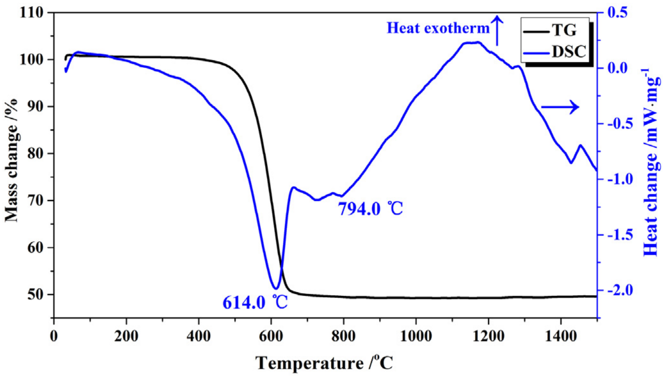

Fig. 2. Thermal analysis results of magnesite.

Subsequently, Yin et al. [11] proposed a novel method for preparing a lightweight corundum-spinel refractory with a density gradient of 2.3–2.65 g/cm^3, apparent porosity of 28–37%, and a high compressive strength of ~82 MPa. The density gradient structure was obtained by the carbothermal reduction of MgO and the subsequent reaction between MgO and Al_2O_3. Furthermore, Hisashi [5] fabricated lightweight corundum aggregates with a bulk density of 3.36 g/cm^3, and used them to prepare lightweight Al_2O_3–MgO–C bricks. The thermal conductivity of these bricks was 20% lower than conventional bricks, with almost no decline in strength.

Current studies focus on the fabrication of lightweight aggregates for Al_2O_3-based, spinel-based or Al_2O_3-spinel based refractories. However, fabrication of lightweight magnesia aggregates has not been widely reported or studied. Magnesia is a crucial refractory raw material with a high softening temperature of 2800 °C and excellent slag resistance and mechanical strength [12]. However, one of its main drawbacks is its high thermal conductivity, which causes significant heat loss. Pores in existing lightweight aggregates are normally micro-sized, and while their properties such as slag resistance and strength are beneficial, they still require further improvement for large-scale commercial applications. Smaller pores (such as nano-sized pores) are believed to reduce thermal conductivity more efficiently, without significantly decreasing the strength or corrosion resistance of lightweight refractories [3,8].

The lightweight magnesia based aggregates can be applied as work lining refractories in refining ladle, steelmaking converter, steelmaking tundish, cement rotary kiln, etc., which are able to decrease the heat loss effectively meanwhile possessor high strength and corrosion resistance against molten slag. In this study, to prepare lightweight magnesia based aggregates with low thermal conductivity, magnesite is used as the raw material, with the addition of nano-sized Al_2O_3 and ZrO_2 particles. Unlike conventional lightweight aggregates, nano-sized pores in the lightweight magnesia aggregates are aimed to be formed. The properties of the aggregates and the microstructure, observed by SEM

Table 2
Initial compositions and treatment method of samples.

Sample no.	S0	S1	S2	S3
Magnesite/wt%	100	96.5	99.5	100
Al_2O_3/wt%	0	3	0	0
ZrO_2/wt%	0	0.5	0.5	0
Water/wt%	0	+60	+60	+60
Ball-milling time/min	0	30	30	30