PREPARATION OF PERICLASE-MAGNESIUM ALUMINATE SPINEL CERAMICS FROM RAW AMORPHOUS MAGNESITE AND ALUMINUM OXIDE NANOPOWDERS

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Abstract

Refractories play an important role in metallurgical, glassmaking and ceramic industries, where they are formed into a variety of shapes to line the interiors of furnaces or kilns or other devices for processing the materials at high temperatures. Many of the scientific and technological inventions and developments would not have been possible without refractory materials. The performance of refractories greatly depends on the selection of raw materials. In this study, raw amorphous magnesite and γ- Al_2O_3 nanopowders were used as starting materials for preparation of periclase-magnesium aluminate spinel ceramics. Magnesite was annealed at a temperature of 800°C with an exposure of 2 hours. A nanosized γ - Al_2O_3 powder was obtained by hydrothermal method. The resulting caustic magnesite and seven volume percent of γ - Al_2O_3 nanopowders were mixed and milled in a ball mill during 30 min. Specimens of periclase-magnesium aluminate spinel ceramics were compacted by a bi-directional axial compression and sintered at 1500°C with an exposure 2 hours at the maximum temperature. The microstructure and mechanical properties of the ceramics were evaluated. Dense periclase-magnesium aluminate spinel ceramics with density of 3.3 g/cm^3 and compressive strength of more than 300 MPa were obtained. The evaluation of the results is the basis for the industry design of magnesia spinel refractories for new advanced applications.

Keywords: amorphous magnesite, periclase, magnesium aluminate spinel, ceramics.

INTRODUCTION

Refractories play an important role in metallurgical, glassmaking and ceramic industries [1,2]. The main problems faced in steel ladle refractories are corrosion by steel slags, abrasion by liquid metal, thermal spalling, oxidation of carbon layer, deterioration of strength at high temperature and molten steel penetration [3-5]. The basic problems in the technology of highly refractory ceramics include of increasing the thermal shock resistance, reducing creep at elevated temperatures, and improving the sinterability of the materials. The performance of refractories greatly depends on the selection of raw materials. It is now well established that magnesia-spinel refractories derived from pure raw materials with a high degree of direct bonding of MgO-MgO and MgO-spinel grains exhibit high hot temperature strength, an improved resistance to slag attack, and dimensional stability at high temperatures [6-8]. In this study, raw amorphous magnesite and γ-Al_2O_3 nanopowders were used as starting materials for preparation of periclase-magnesium aluminate spinel ceramics.

1. EXPERIMENTAL

1.1 Materials

In this study, raw amorphous magnesite (Khalilovo deposit) and γ- Al_2O_3 nanopowders were used as starting materials for preparation of periclase-magnesium aluminate spinel ceramics. Amorphous magnesites of the Khalilovo deposit are widely distributed in the Southern Urals (Russia).

1.2 Apparatus and Procedures

It is known that the impurities present in raw materials can ultimately affect the quality of refractory products, the extent of their application area, and their lifespan [9]. The samples of raw amorphous magnesite were first crushed by a jaw crusher. The particle size was thereby reduced to nearly 2 mm. The pulverized powders were sieved by means of vibrating sieves and classified into different particle sizes. Then magnetic separation technique was applied to investigate the dressability of raw amorphous magnesite. The content of $MgCO_3$ is 95% in the magnesium carbonate concentrate. The magnesium carbonate concentrate obtained was calcined at a temperature of 800°C with an exposure of 2 hours. The magnesite transformed into caustic magnesia by thermal decomposition:

$$MgCO_3 \xrightarrow{900^\circ C} MgO + CO_2 \qquad (1)$$

A nanosized γ - Al_2O_3 powder was obtained by hydrothermal method (hydrothermal decomposition of aluminum hydroxide) [10]. The resulting caustic magnesia and seven volume percent of γ - Al_2O_3 nanopowders were mixed and milled in a ball mill during 30 min. Specimens of periclase-magnesium aluminate spinel ceramics were compacted to form a cylinder (diameter 21 mm, height 10 mm) by a bi-directional axial compression without binder with the use of the hydraulic pelletizing press Herzog TP40/2d. Then obtained samples were sintered at 1500°C with an exposure 2 hours at the maximum temperature. As a result samples of periclase-magnesium aluminate spinel ceramics were obtained.

Phase composition of raw amorphous magnesite was determined by the X-ray phase analysis method (diffractometer Rigaku Ultima IV; CuKα – emission (radiation), Ni – filter). Examinations of the elemental composition were carried out by using electron ion microscope Quanta 200 3D and Nova NanoSEM (SEM). To determine the precise material ultimate composition of periclase-magnesium aluminate spinel ceramics, X-ray spectral analysis with the use of scanning electron microscope Quanta 200 3D was performed. The determination of nanosized γ - Al_2O_3 powder particle size was performed with the use of transmission electron microscope JEOL JEM 2100 (TEM). A volume helium pycnometer (AccuPyc II 1340, Micromerltics Ltd.) was used to measure the density of the periclase-magnesium aluminate spinel ceramics. Mean values and standard deviations were determined from five successive measurements. The temperature and sintering of the sample's behavior were determined by means of the high temperature dilatometer Netzsch L75H. The heating was performed at the temperatures ranging from 20 to 1550ºC at a rate of 2ºC/min. Microhardness of the ceramic samples was determined by an automatic microhardness tester DM-8B (Affri) by Vicker's test at a test load of 500 g. Indentation was carried out with the distance between the indents being 20 μm. On an average, 10 tests were used as an indicator of the sample hardness. The uni-axial compressive tests were carried out in air at ambient temperature by means of testing machine Instron 300LX.

2. Results and Discussion

The phase composition of raw amorphous magnesite is listed in Table 1.

Table 1 Phase composition of raw amorphous magnesite

	$Mg(CO_3)$	$Mg_6Si_4O_{10}(OH)_8$	$CaCO_3$	Fe_3O_4
Main phases, %	97.3	1.2	0.9	0.6

The results of the study of nanosized γ - Al_2O_3 powder with the use of transmission electron microscopy are shown in Fig. 1.

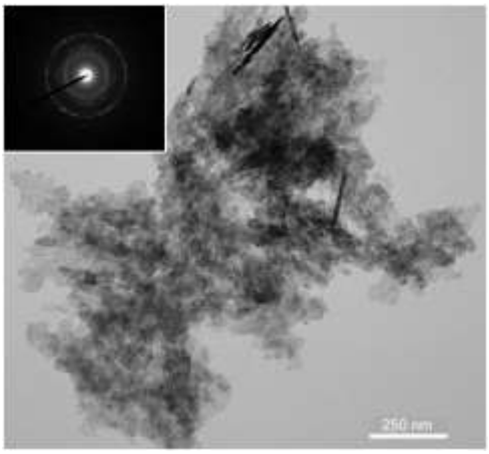


Fig. 1 TEM micrographs and electron diffraction pattern (inset) of nanoparticles of γ - Al_2O_3 powder

The behavior of the compacted powder of caustic magnesia during firing was investigated by dilatometry, which recorded the shrinkage values of the bodies in dependence on temperature. The results of thermomechanical analysis at temperatures from 20 to 1550ºC are shown in Fig. 2.

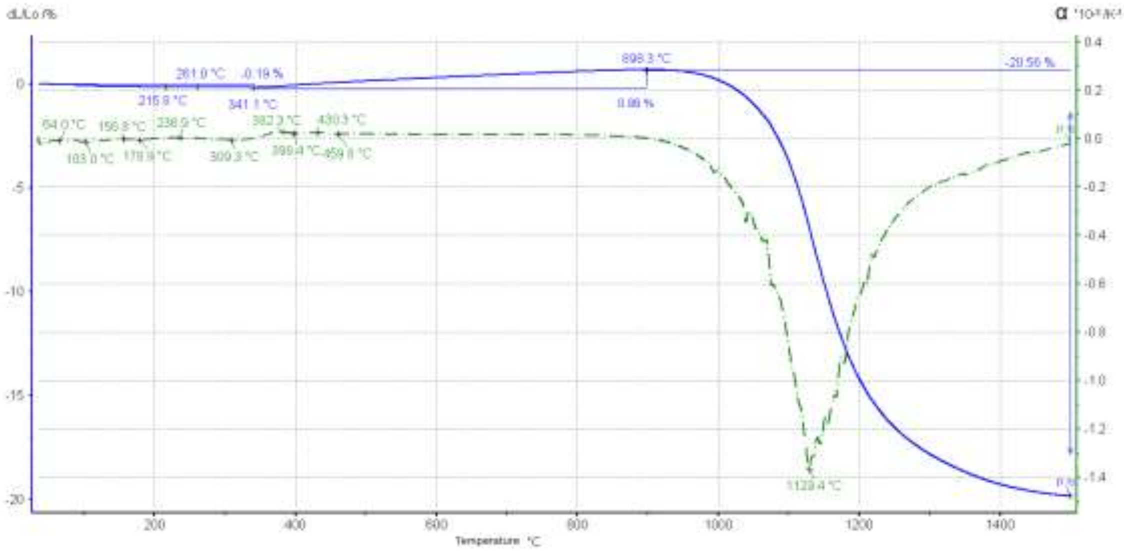
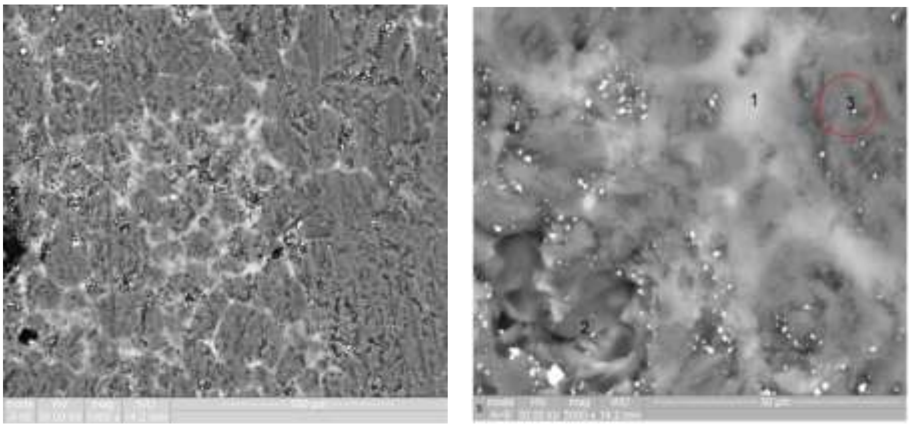


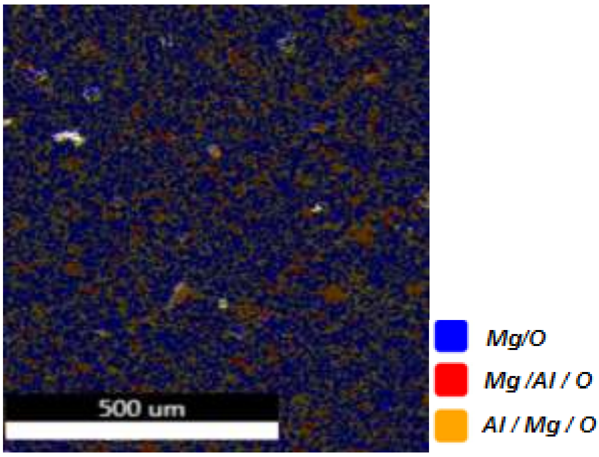
Fig. 2 Dilatometric curve for compacted powder of caustic magnesia

It was established that appreciable compaction of the compacted material starts at 1000°C. The maximum rate of shrinkage is at 1500°C, i.e., the most intense sintering of the material occurs. Microscopic analysis of samples of periclase-magnesium aluminate spinel ceramics was conducted using Quanta 200 3D and Nova NanoSEM 450 scanning electron microscopes (Fig. 3). The samples exhibit a quite dense structure.



(a)

Point 3	
Element	Mol.%
MgO	96.26
Al_2O_3	1.21
SiO_2	1.21



(b) (c)

Fig. 3 SEM micrograph (a), element composition (b) (Quanta 200 3D) and SEM EDX element distribution maps (NanoSEM 450) (c) of samples of periclase-magnesium aluminate spinel ceramics

The $MgAl_2O_4$ completely enclose the periclase crystals, binding them firmly together, and hence, forming a very strong mass (Fig. 3). The density of the samples of periclase-magnesium aluminate spinel ceramics is 3.3 g/cm^3, which correlates well with the theoretical density of alumina-magnesium spinel. The samples of periclase-magnesium aluminate spinel ceramics exhibited a high hardness of about 742 $HV_{0.5}$ and compressive strength of more than 300 MPa.

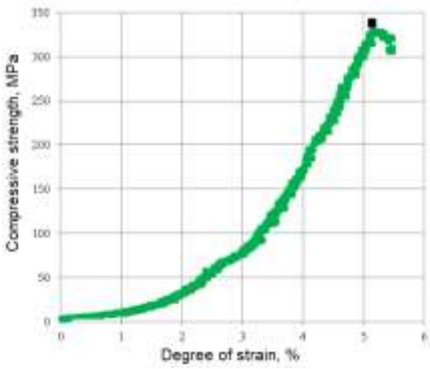


Fig. 4 Compression strength test of samples of periclase-magnesium aluminate spinel ceramics

CONCLUSION

Dense periclase-magnesium aluminate spinel ceramics with density of 3.3 g/cm^3 and compressive strength of more than 300 MPa were obtained. The evaluation of the results is the basis for the industry design of magnesia spinel refractories for new advanced applications.

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