Effect of Different Crystal Form Nanometre Zirconia on Thermal Shock Resistance of Magnesia Ceramic

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Abstract. The magnesia ceramic specimens were prepared using high purity magnesia powder, monoclinic nanometre zirconia, tetragonal nanometre zirconia, cubic nanometre zirconia as starting materials in order to improve thermal shock resistance of magnesia ceramic. The specimens were sintered at 1550°C for 2 hours under air atmosphere. The thermal shock resistance and sintering property of magnesia ceramics with different crystal nanometre zirconia additives were investigated. The results show that density of the specimens with zirconia is improved due to the dispersal distribution of zirconia in periclase grain boundary. The sintering property of magnesia with zirconia additives are considerably promoted. The thermal shock resistance of the specimens with tetragonal zirconia or cubic zirconia is improved due to second crystalline phase toughening mechanism of zirconia .Thermal shock resistance of specimens with monoclinic zirconia is improved due to phase transformation toughening mechanism and second crystalline phase toughening mechanism of zirconia.

1. Introduction
The Magnesia ceramic crucible has excellent thermo-chemical properties and resistance to corrosion of molten metals. It can be used as containers for smelting rare metals, zinc, copper, lead, platinum, cobalt and their alloys. It can also be used as a casting die for casting pure metals and crucible for melting Au-B alloys in semiconductor processes. It is the key material in modern metallurgical industry. At present, graphite crucible is commonly used in smelting rare metals. The inner wall of graphite crucible is easy to fall off and enter into rare metals in the process of high temperature smelting, which affects the quality of metals and is difficult to meet the requirements of actual production [1].Magnesia ceramics have excellent high temperature performance in smelting rare metals, however improving high temperature performance, especially thermal shock resistance, is the technical bottleneck of replacing graphite crucible with magnesia ceramic crucible.

The martensitic transformation of zirconia (tetragonal zirconia shorted as t-ZrO$_2$ to monoclinic zirconia shorted as m-ZrO$_2$) can absorb energy, slow stress concentration at crack tip, prevent crack propagation and improve toughness of ceramics [4-7]. Some research shows that the thermal shock resistance [3,8-10] or sintering properties [11] of magnesia material can be improved by adding zirconia. There are few reports on improving thermal shock resistance of magnesia ceramics by adding zirconia at present. In this paper, nanometre zirconia powders with monoclinic, tetragonal and cubic crystal forms were used as additives to study the effect of zirconia crystal forms on thermal shock resistance of magnesia ceramics, in order to provide technical support for the preparation of magnesia ceramic crucibles.
2. Experiment

2.1. Starting material
The main raw materials used in the experiment are high purity magnesia powder (particle size 40-60 nm), m-ZrO₂ nanopowder (particle size 20-40 nm), t-ZrO₂ nanopowder (particle size 20-40 nm) and cubic zirconia (shorted as c-ZrO₂) nanopowder (particle size 20-40 nm). The chemical composition is shown in Table 1. The phase compositions of three different crystal forms nanometre ZrO₂ powders are shown in Figure 1.

| Raw material   | ZrO₂ | MgO | Y₂O₃ | SiO₂ | Fe₂O₃ | CaO | Na₂O | LOI  |
|----------------|------|-----|------|------|-------|-----|------|------|
| High purity magnesia | 0.00 | 99.54 | 0.00 | 0.08 | 0.06  | 0.03 | 0.16 | 0.13 |
| m-ZrO₂         | 99.82 | 0.02 | 0.00 | 0.03 | 0.01  | 0.01 | 0.02 | 0.09 |
| t-ZrO₂         | 94.39 | 0.03 | 5.35 | 0.04 | 0.03  | 0.02 | 0.06 | 0.08 |
| c-ZrO₂         | 91.04 | 0.02 | 8.73 | 0.03 | 0.02  | 0.03 | 0.04 | 0.09 |

![XRD patterns of three nanometre zirconia powders with different crystal form.](image)

Figure 1. XRD patterns of three nanometre zirconia powders with different crystal form.

2.2. Specimens preparation
The specimen prepared by high purity magnesia powder were marked as M. According to 86% (w) high purity magnesia powder and 14% (w) m-ZrO₂ nanopowder or t-ZrO₂ nanopowder or c-ZrO₂ nanopowder, the specimens were marked as MZ, TZ and CZ, respectively. The batched material was put into a planetary ball mill for 12 hours by wet milling, in which the mass ratio of material, ball and alcohol was 1:1.5:2. The slurry after ball milling was put into the drying box and dried at 60 degree Celsius for 12 hours. The dried slurry was ground in agate and then sifted through 80 meshes sieves. The sifted material was dry-pressed with 769YP-24B presser under 200 MPa for 30 seconds, and the specimens with diameter 20mm and height 4mm were formed. The formed specimens were dried in drying box at 110 degree Celsius for 24 hours. The dried specimens were sintered in electric furnace at 1550 degree Celsius for 2 hours, and then cooled to room temperature naturally with the furnace.
2.3. Characterization
The bulk density and apparent porosity of sintered specimens were measured according to GB/T 25995-2010 Test Method for Density and Apparent Porosity of Fine Ceramics, and the linear shrinkage change rate after sintering was calculated according to the diameter of specimens before and after sintering. The phase composition of the sintered specimens were measured by X-ray diffractometer (Cu target, tube voltage 40 kV, tube current 40 mA, step length 0.013 degrees, scanning range 10-90 degrees). The microstructures of the sintered specimens were observed by field emission scanning electron microscopy (FESEM). The thermal shock resistance of specimens were tested by water-cooling method. The sintered specimens were placed in a muffle furnace at 900 degree Celsius for 30 minutes at first. The specimens were taken out immediately and quenched in flowing water to room temperature to observe whether there were cracks in the specimens. Repeat this process until cracks appear in the specimen.

![Graph of bulk density and apparent porosity](image)

(a) Bulk density and apparent porosity of sintered specimens

![Graph of linear shrinkage rate](image)

(b) Linear shrinkage rate of specimens

Figure 2. Effect of different crystal form on bulk density, apparent porosity and linear shrinkage rate of sintered specimens.
3. Results and discussion

3.1. Sintering property
Figure 2 shows the bulk density, apparent porosity and linear shrinkage rate of specimens sintered at 1550 degree Celsius. The bulk density and apparent porosity of the specimens increased by adding ZrO2 compared with those without adding ZrO2. The bulk density of the specimens with adding m-ZrO2 was the largest and the apparent porosity was the smallest as showed in Figure 2 (a). It can be seen from Figure 2 (b) that all specimens shrink after sintering. Among them, the maximum shrinkage rate is 21.4% when m-ZrO2 is added. It can be seen that the addition of ZrO2 promotes the sintering of magnesia ceramics and improves their density.

3.2. Thermal shock resistance
Figure 3 shows the thermal shock resistance test results of sintered specimens. It can be seen that the thermal shock resistance of specimens without ZrO2 is very poor, and the thermal shock resistance of specimens with different crystal forms of ZrO2 is obviously improved. Among them, the specimen with m-ZrO2 has the best thermal shock resistance, and the times of thermal shock cycles reaches 8 times. It can be seen that the addition of ZrO2 can improve the thermal shock resistance of magnesia ceramics as well as the sintering property.

![Figure 3. The times of thermal shock cycles of sintered specimens.](image)

3.3. Phase composition and microstructure analysis
Figure 4 shows the XRD patterns of sintered specimens with different crystal forms ZrO2. It can be seen that the main crystalline phase of all specimens is periclase. No crystal transformation of ZrO2 is observed in the specimens with c-ZrO2 and the specimens with t-ZrO2. Most m-ZrO2 of the specimens with m-ZrO2 transform to c-ZrO2 and t-ZrO2, which indicate that Zr^4+ in ZrO2 is replaced by Mg^2+, c-ZrO2 solid solution and t-ZrO2 solid solution are formed in the specimens with m-ZrO2.[12]

Figure 5 shows the microstructure images of the sintered specimens. In the specimen marked M without ZrO2, the gray periclase grain size is 2-30 micron, the periclase grain size distribution is not uniform, and there are many abnormal growth periclase grains. In the specimens with ZrO2, the fine and uniform white grains are ZrO2 grains, which are dispersed among the periclase grains and have close bonding between the periclase grains. The abnormal growth of periclase grains is obviously
inhibited, the narrow grain size distribution is formed, and the uniformity of microstructure is improved. The periclase grain size of the specimen with m-ZrO$_2$ is between 1 and 8 microns, the ZrO$_2$ grain size is less than 2 microns. The periclase grain size of the specimen with t-ZrO$_2$ is 1 to 5 microns, the ZrO$_2$ grain size is less than 2 microns. The periclase grain size of the specimen with c-ZrO$_2$ is 2 to 10 microns, the ZrO$_2$ grain size is less than 2 microns.

![XRD patterns of sintered specimens.](image)

**Figure 4.** XRD patterns of sintered specimens.

![Microstructure images of sintered specimens.](image)

**Figure 5.** Microstructure images of sintered specimens.

The nanometre ZrO$_2$ added in the specimen disperses at the grain boundary of periclase, which prevents the abnormal growth of periclase grain, prevents the fusion of periclase grain boundary, and promotes the pore diffusion and discharging [13]. The density of the specimens with ZrO$_2$ increase. The solid solution is formed between ZrO$_2$ and MgO in the specimen with m-ZrO$_2$ [14]. Cationic vacancies are generated in the lattice of periclase, which activates the lattice of periclase, increases the surface energy of grain boundary, greatly promotes the sintering of magnesia ceramics and increases the bulk density of magnesia ceramics.

The density and microstructure uniformity of the specimens with nanometre ZrO$_2$ are improved, the strength and toughness of them are improved correspondingly, and the thermal stress resistance is enhanced [3]. Therefore, the thermal shock resistance of the specimens with nanometre ZrO$_2$ is better than that of the specimens without ZrO$_2$. Although ZrO$_2$ in the specimens with nanometre t-ZrO$_2$ and nanometre c-ZrO$_2$ has no phase transformation, because ZrO$_2$ belongs to the second phase and disperses between periclase grains, micro-cracks occur near ZrO$_2$ grains during sintering and cooling due to the mismatch of thermal expansion coefficient and elastic modulus between ZrO$_2$ and magnesia.
During thermal shock test, thermal shock cracks deflect, branch or bend along micro-cracks, which extend the crack propagation path [15]. The fracture surface energy is increased. The thermal shock resistance of the specimens is improved. In the specimens with m-ZrO$_2$, m-ZrO$_2$, t-ZrO$_2$ and c-ZrO$_2$ disperse among the periclase grains. In addition to the second phase toughening mechanism, martensitic transformation of t-ZrO$_2$ into m-ZrO$_2$ occurs during sintering and cooling, accompanied by 3%-5% volume expansion [16], resulting in micro-cracks around m-ZrO$_2$ grains. During the thermal shock test, when the micro-cracks are in the acting zone of thermal shock crack, they absorb the energy for thermal shock crack propagation, reduce the concentration of thermal stress and effectively restrains the crack propagation. The composite toughening of phase transformation toughening mechanism and second phase toughening mechanism greatly improves the thermal shock resistance of specimens.

4. Conclusions
(a) The added nanometre ZrO$_2$ disperses at the grain boundary of periclase, inhibits the abnormal growth of periclase grain, improves the uniformity of microstructure, promotes the pore diffusion and discharges inside the specimens, and improves the density of the specimens. The solid solution of ZrO$_2$ and magnesia is formed in the specimens with m-ZrO$_2$, which activated the crystal lattice of periclase and greatly promoted the sintering property of magnesia ceramics.
(b) ZrO$_2$ in the specimens with t-ZrO$_2$ and c-ZrO$_2$ dispersed by the second phase between the periclase grains to form micro-cracks, which increase the thermal shock crack propagation path and improved the thermal shock resistance of the specimens.
(c) In addition to the second-phase toughening mechanism, martensitic transformation of ZrO$_2$ occurs during sintering and cooling, resulting in micro-cracks. The energy required for thermal shock crack propagation is absorbed during thermal shock test. The thermal shock resistance of the specimens is improved by the combination of the phase transformation toughening mechanism and the second phase toughening mechanism.

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