Migration and solid solution of stabilizer MgO in PSZ ceramic

Liang Zhao^{1,a}, Qunhu Xue^{1, 2, b}

¹ College of Materials and Mineral Resources, Xi'an University of Architecture and Technology,
Xi'an 710055, China;

² Shaanxi Techno-institute of Recycling Economy, Xi'an 710055, China.

^ajrzhaliang@163.com, ^bxuequnhu@xauat.edu.cn

Keywords: partially stabilized zirconia, zirconia stabilizer, solid solution, migration

Abstract. The partially stabilized zirconia ceramic samples were fabricated using MgO stabilizer. The solid solution and migration process of stabilizers in zirconia grains under working temperature was studied by XRD, SEM and EDS. Results show that after 1710 °C×2 h sintering, MgO stabilizer in the sample didn't solid-solute completely, part of MgO enriched in the position of the impurity SiO₂ to generating forsterite, stability of zirconia grains didn't reach highest; With increasing heat preservation time under working temperature 1540 °C, solid solution of stabilizer and zirconia stabilization completed in 8 h.

1. Introduction

The partially stabilized zirconia after stabilizing treatment has good toughness and volume stability, can be widely used in high-performance structural ceramics field and also the main raw material of metering nozzle which is the key functional device of continuous casting^[1]. Common zirconia stabilizers include MgO, Y₂O₃, CaO, CeO, etc^[2]. Due to the radius of these cations are closer with Zr⁴⁺ ionic radius, so they can dissolve in ZrO₂ at high temperatures, and generate solid solution with ZrO₂ to avoid precipitating during the cooling process. This makes zirconia can maintain high temperature phase below the phase transition temperature^[3,4].

In this paper, MgO was added in monoclinic zirconia powder as stabilizer. In accordance with the firing schedule of zirconia metering nozzle, stabilized zirconia ceramic specimen were fabricated after sintering at 1710 °C for 2 h. After 1540 °C(service temperature of metering nozzle) heat preservation for different time, the specimens were cooled by water quenching. Then the distribution of stabilizer and mineral phase of specimens were characterized through XRD, SEM and EDS. Analysis on the process of stabilizer MgO migrating and solid soluting in ZrO₂ ceramic can provide important foundation for the research of the zirconia ceramic stabilization.

2. Experiment

The chemical composition of raw material was shown in Table 1.

Table 1 Chemical composition of raw material

Specimen	ZrO ₂	HfO ₂	MgO	Y ₂ O ₃	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
A	94.35	2.09	2.8	-	0.07	0.46	0.15	0.08
B	95.07	1.95	2.2	-	0.08	0.53	0.13	0.04

Specimen A and B were fabricated through compression molding, 300 MPa compressed into φ50×10 mm cylindrical specimens, sintering at 1710 °C for 2 h. In order to illustrate the migration and solution process of stabilizer MgO in the zirconia material, the ceramic specimens after sintering were cooled by water quenching after heat preservation for 0~12 h in high temperature furnace at 1540 °C (service temperature of zirconia metering nozzle). The specimen before sintering is K, the specimens after sintering are A0, A4, A8, A12, B0, B4, B8, B12.

Analyze mineral phase and microstructure of the specimens after heat preservation for 0~12 h at 1540 °C by D/MAX 220 X-ray diffractometer and Quanta 200 scanning electron microscope.

3. Results and discussion

3.1 phase composition

XRD patterns of specimen A and B after heat preservation for 0~12 h were shown in Figure 1.

Fig. 1 The XRD spectra of the specimen A and B

From Figure 1, it can be seen that the mineral phase of specimens A and B are mainly composed of monoclinic zirconia before sintering, meanwhile monoclinic and cubic zirconia after sintering. After heat preservation for a certain time at 1540 °C, through comparison of diffraction peak of each specimen in the vicinity of $2\theta=30^\circ$, it can be found that the relative intensity of diffraction peak of cubic phase in specimen A and B gradually increased, that of monoclinic phase gradually decreased with the increase of heat preservation time.

The volume fraction of monoclinic phase can be obtained by the following formula (1) [5,6]:

$$V_m = \frac{1.6031I_m(111)}{1.6031I_m(111)+I_c(111)} \quad (1)$$

(I_m and I_c are the intensity of monoclinic phase and cubic phase.)

The results were shown in Figure 2.

Fig. 2 The XRD analysis results of specimens

The mineral composition results of each specimen are shown in Figure 2. It can be found that the stability degree of zirconia is very sensitive to the content of stabilizer MgO, resulting in the relative content of m-ZrO₂ and c-ZrO₂ in specimens A and B markedly different. However the mineral phase of specimens A and B don't change after 8 hours heat preservation.

3.2 microstructure changes

In order to characterize the migration and solid solution process of stabilizer MgO in zirconia ceramic during the heat preservation process, the results of energy spectrum analysis on specimen A were shown in Figure 3 and Table 2.

Fig. 3 The EDS results of specimen A after
Table 2 EDS result of specimens (atom %)

Element	1	2	3	4	5	6	7	8
Zr	8.8	3.7	2.6	0	36.9	40.1	47.6	46.5
Mg	27.3	34.1	32.7	35.6	2	3.1	4.1	4.2
Si	13.8	19.1	21.2	23.2	0	0	0	0
O	50.2	43.1	43.6	41.2	61.1	56.7	48.3	49.3

It can be seen from the position 1~4 in the specimen A, after 1710 °C firing, a part of the MgO didn't dissolve in zirconia grains, but concentrated in the location where SiO₂ (impurity of zirconia raw material) existed. The zirconia raw material in this experiment was monoclinic zirconia which was prepared by zircon (ZrSiO₄) desilication by plasma method. The preparation method determines a small amount of SiO₂ residues in raw material can't be removed completely. The dark mineral phase in location 1 was forsterite (2MgO•SiO₂) concluding from Mg/Si atomic ratio. With the increase of heat preservation time, Mg/Si ratio decrease from position 1 to 4. This showed that 2MgO•SiO₂ partially turn into MgO•SiO₂ and MgO. From position 5 to 8, it can be seen that MgO content in zirconia increased with the heat preservation time prolonging. It showed that the MgO decomposed from 2MgO•SiO₂ dissolved into the ZrO₂ grains again. The increasing of stabilizer content in grains will lead to m-ZrO₂ transformation to c-ZrO₂. This is consistent with the previous results of XRD.

Due to the specimen A and B are both stabilized by MgO, so the distribution of the stabilizer could be characterized by specimen A. Figure 5 is the stabilizer distribution map of specimen A after heat preservation at 1540°C.

Fig. 4 The distribution of the stabilizer in the specimen A

In Figure 4, with the increase of heat preservation time at 1540°C, the distribution of dark mineral phase gradually become well punctate from reunite state. This change is obvious in the specimen A and B. This shows that in specimen A and B there was a part of stabilizer MgO enriching in the location of impurity SiO₂ to generate forsterite(2MgO•SiO₂), not dissolved into the zirconia grains. After heat preservation at 1540°C, part of forsterite gradual decompose to MgO which migrated again and dissolve in zirconia particles to form a certain amount of solid solution.

4. Summary

(1) After sintering at 1710 °C for 2 h, stabilizer migration and solid solution didn't reach a uniform state in MgO stabilized zirconia ceramic specimens, a part of stabilizer MgO will enrich in the position of SiO₂ impurity to generate the forsterite (2MgO•SiO₂), zirconia grains didn't fully and achieve the highest stability.

(2) With the preservation at service temperature 1540°C, the distribution of the stabilizer enriched position gradually become well punctate from reunite state. The migration and solid

solution of MgO stabilizer in the specimen and stabilization of the zirconia grains will be completed in 8 h;

(3) Impurity SiO_2 in the raw materials of zirconia can lead to the exsolution of stabilizer MgO, which affects the stability of zirconia ceramic.

Acknowledgement

The present work is supported by the funds of the National Natural Science Foundation of China (51372193) and the Natural Science Basic Research Plan in Shaanxi Province of China (2014JM6224).

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