Preparation and characterization of ceria partially stabilized zirconia ceramics

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Abstract. The ceria partially stabilized zirconia (Ce-PSZ) ceramics with 7wt%, 10wt%, and 13wt% CeO₂ stabilizing agent were prepared under industrial conditions. The relationship between the content of CeO₂ and the physics property, mineral composition, and microstructure of zirconia metering nozzles was investigated through X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The results show that with the increasing content of CeO₂, the apparent porosity of samples increases, the bulk density and compressive strength decreases, the thermal shock resistance first increases and then decreases; meanwhile, m-ZrO₂ is transformed into c-ZrO₂ and the degree of stability is improved. However, excess c-ZrO₂ will lead to abnormal growth of zirconia particles, which lead to reduction of compressive strength and apparent porosity increasing. Thermal shock resistance of Ce-PSZ is sensitive to the addition of CeO₂. The best thermal shock resistance can be obtained with the addition of 10wt% CeO₂ stabilizing agent, which is 1.5 times that of the sample with 7wt% CeO₂ and 3 times that of the sample with 13wt% CeO₂.

1. Introduction

Partially stabilized zirconia is widely used as tundish refractory in continuous casting for its excellent properties, such as high melting point, low thermal conductivity, good thermal shock resistance, and remarkable strength [1, 2]. As the technology development of continuous casting, the requirements for long service life of refractory are even more demanded. In view of the expansion, cracking, and other damage phenomena of the PSZ refractory during casting, an effective way to improve the performance of the tundish refractory is to select new materials and formulations with good physical property and thermal shock resistance.

The preparation and properties of Mg, Ca or Y-PSZ have been well investigated. However, to data, the research of Ce-PSZ ceramic is not well carried out. In this paper, Ce-PSZ ceramics with 7wt%, 10wt%, and 13wt% CeO₂ stabilizing agent were prepared under industrial conditions, the relationship between the content of CeO₂ and the physics property, mineral composition, and microstructure of zirconia metering nozzles was investigated, which provide a basis for prolonging the service life of the zirconia-base refractory.
2. Experimental Method and Process

2.1. Raw materials
PVA solution (5wt %) as binding agent, CeO$_2$ powder (AR) as stabilizing agent, and monoclinic zirconia powder (average particle size is 7.51μm) as raw material, which the chemical and phase composition are shown in Table 1 and Figure 1.

| Composition       | ZrO$_2$ | MgO | CaO | SiO$_2$ | Al$_2$O$_3$ | Na$_2$O | Fe$_2$O$_3$ | TiO$_2$ | IL |
|-------------------|---------|-----|-----|---------|-------------|---------|-------------|---------|----|
| Zirconia powder   | 97.36   | 0.14| 0.16| 0.35    | 0.34        | 0.38    | 0.08        | 0.09    | 1.1|

Figure 1. XRD results of monoclinic zirconia.

2.2. Preparation and characterization
Ce-PSZ ceramics samples C$_{07}$, C$_{10}$, and C$_{13}$ with 7wt%, 10wt% and 13wt% CeO$_2$ addition were prepared under industrial conditions: molding pressure 300 MPa, sintered at 1710°C for 2h. The mineral composition was investigated through X-ray diffraction (D/MAX 220), the anode material is Cu, accelerating voltage and electricity is 45KV, 80mA, scanning speed is 16°/min with 0.02° increments for step-scan. The microstructure was observed by scanning electron microscopy (Quanta 200).

3. Results and Discussion

3.1. Mineral Composition Analysis
The mineral compositions of various sintered Ce-PSZ samples are shown in Figure 2.
Figure 2. XRD results of various sintered samples.

Figure 2 shows that mineral composition of samples C\textsubscript{07}, C\textsubscript{10}, C\textsubscript{13} were composed of cubic phase (c-ZrO\textsubscript{2}) and monoclinic phase (m-ZrO\textsubscript{2}), and the diffraction peak of tetragonal phase zirconia did not appear. The reason is that radius of Ce\textsuperscript{4+} is similar to that of Zr\textsuperscript{4+}, and Ce\textsuperscript{4+} has a high solubility in zirconia. When samples are sintered at high temperature, atom Ce\textsuperscript{4+} has displacement reaction with Zr\textsuperscript{4+} and forms solid solution with zirconia. When the sample drops from high temperature to low temperature, the difficulty of particle Zr\textsuperscript{4+} rearrangement is increased due to Ce\textsuperscript{4+} in solid solution [3, 4], which makes zirconia still maintain high-temperature phase to room temperature[5].

Stability degree of sintered samples can be measured by the phase component. The following formula was used to compute content of monoclinic and cubic phase in the samples [6].

\[
V_m = \frac{1.603 I_m(111)}{1.603 I_m(111) + I_c(111)}
\]

\(I_m\): The diffraction intensity of monoclinic phase.
\(I_c\): The diffraction intensity of cubic phase.
\(V_m\): Volume fraction of monoclinic phase.
\(V_c\): Volume fraction of cubic phase.

Volume fraction of monoclinic phase in sample C\textsubscript{07} was calculated about 50%; Volume fraction of monoclinic phase in sample C\textsubscript{10} was calculated about 26%; Volume fraction of monoclinic phase in sample C\textsubscript{13} was calculated about 12%.

3.2. Physical performance

Physical properties of samples were shown in Table 2.

| Sample | Bulk density /g.cm\textsuperscript{-3} | Apparent porosity /% | Compressive strength /MPa | Thermal shock resistance /times |
|--------|-------------------------------------|----------------------|---------------------------|---------------------------------|
| C\textsubscript{07} | 5.16 | 11.71 | 343.23 | 5 |
| C\textsubscript{10} | 5.08 | 13.31 | 264.45 | 12 |
| C\textsubscript{13} | 4.93 | 15.92 | 228.65 | 8 |
With the increasing of CeO$_2$ stabilizing agent, apparent porosity of samples increases, bulk density and compressive strength decreases, thermal shock resistance first increases and then decreases. Too much or too little content of cubic phase means stability degree of sintered samples is too high or too low, which is not beneficial for thermal shock resistance of samples. Thermal shock resistance keep a high level when content of cubic phase is around 70%. The main reason is the martensitic transformation between c-ZrO$_2$ and m-ZrO$_2$, which accelerate the formation of micro-cracks within the products. Micro-cracks can release elastic energy to restrain the crack propagation and improve thermal shock resistance. Appropriate porosity is also good for thermal shock resistance due to dispersing the path of crack propagation. Chen proved samples composed of 30% monoclinic phase and 70% cubic phase obtain the best performance of thermal shock resistance [7]. Monoclinic zirconia content had been calculated according to the formula 1. Monoclinic phase content in sample C$_{10}$ is closest to 30% and sample C$_{10}$ possessed moderate porosity, which can provide the highest thermal shock resistance.

3.3. Microstructure Analysis

The microstructure of sample C$_{07}$, C$_{10}$, and C$_{13}$ was analysed further by scanning electron microscopy, Figure. 3 and 4 shows the morphology of sample C$_{07}$, C$_{10}$, and C$_{13}$.

![Sample C$_{07}$](image1)

(a) Sample C$_{07}$

![Sample C$_{10}$](image2)

(b) Sample C$_{10}$

![Sample C$_{13}$](image3)

(c) Sample C$_{13}$

**Figure 3.** Distribution of pores in various samples.
Figure 4. Microstructure of zirconia particles in various samples.

From Figure 3, there are more number of pores in sample $C_{07}$ than $C_{10}$ and $C_{13}$, the distribution of pores is relatively uniform. It can be seen from Figure 4 that for the different content of stabilizing agent, the microstructure of the corresponding samples are different. The zirconia grain size in sample $C_{07}$ is not uniform after being sintered, there is little granular structure, there are few small pores, which makes the thermal shock stability of the sample worse. The microstructure the sample $C_{10}$ is granular, and the zirconia grain size is basically uniform. There are no obvious cracks. This is also the reason why the thermal shock resistance of samples $C_{07}$ and $C_{13}$ are not as good as those of sample $C_{10}$. The morphology of the crystal grains in sample $C_{13}$ is different, the size is not uniform, the bonding between the crystal grains is not dense, some particles grow abnormally, and some pores and cracks existed, which reduce the resistant to thermal shock.

4. Conclusion

With the increasing amount of $\text{CeO}_2$, the apparent porosity of Ce-PSZ ceramics increases, the bulk density and compressive strength decreases, thermal shock resistance first increases and then decreases; meanwhile, $\text{m-ZrO}_2$ is transformed into $\text{c-ZrO}_2$ and the degree of stability is improved.

Excess $\text{c-ZrO}_2$ will lead to abnormal growth of zirconia particles, which lead to reduction of compressive strength and apparent porosity increasing.

Thermal shock resistance of Ce-PSZ is sensitive to the addition of $\text{CeO}_2$. The best thermal shock resistance can be obtained with the addition of 10wt% $\text{CeO}_2$ stabilizing agent, which is 1.5 times that of the sample with 7wt% $\text{CeO}_2$ and 3 times that of the sample with 13wt% $\text{CeO}_2$. 
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