Effect of Manganese Oxide on the Sintered Properties of 8YSZ

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Abstract

The sinterablility of 8 wt. % yttria-stabilized-zirconia (8YSZ) containing different weight ratios of MnO₂ as sintering aid was investigated over the temperature range of 1200-1400°C. Relative density, microstructure, microhardness and bending strength as a function of sintering temperature and sintering aid content were investigated. The experiment results show that the addition of MnO₂ is effective in aiding densification, and the relative density, microhardness and bending strength of doped samples are generally much higher than those of the undoped samples; the relative density, grain size and microhardness increase with the increasing of sintering temperature and addition content of MnO₂; when the additive content of MnO₂ is below 3 wt. %, the bending strength increases with the increasing of sintering temperature and addition content of MnO₂, sintered at 1300°C with 3 wt. % MnO₂ addition, the sample has the maximum bending strength 235.5 MPa, fine grain size and high relative density are two main reasons of the high bending strength and hardness of the materials.

Keywords: Low-temperature sintering; 8YSZ; Microstructure; Mechanical properties; MnO₂

1 Introduction

Typically, 8 wt. % yttria-stabilized-zirconia (8YSZ) are being widely utilized to prepare thermal barrier coatings [1-2], due to its excellent properties. Plasma spraying and chemical/physical vapor deposition [3-4] are currently common industrial practices of 8YSZ thermal barrier coatings. However, they all have limitations for handling axially symmetric and complex-shaped substrates. Slurry spraying coating [5-6] and electrophoretic deposition (EPD) [7-8], provide the potential to fabricate ceramic coatings with the advantages of less restriction in substrate shape, simple equipment requirements and low cost. However, the main problem associated with these processes is the difficulty in sintering of the coatings. Commonly the sintering temperature of 8YSZ is above 1450°C, which is much higher than the serviceability temperature of metal substrates.

Adding sintering aid is a good method to lower the sintering temperature of 8YSZ [9-11]. Many studies have been reported in the literature concerning the effectives of additives on sintering of zirconia composite, e.g. SiO₂ [12], Bi₂O₃ [13], B₂O₃ [14], CAS glass [15], CuO, TiO₂, or MnO₂ [16-17]. Huang [18] got densified 3 mol. % Y₂O₃-stabilized ZrO₂ polycrystals composite at a temperature as low as 1400°C by doping TiO₂-MnO₂. S. Ramesh [19] investigated the effect of small amounts of MnO₂ (~1 wt.%) on the sintered properties of Y-TZP ceramics.

In most cases, the presence of additives resulted in densification of the ceramics via low-temperature sintering. However, low-temperature sintering of 8YSZ with MnO₂ addition has received little attention. The purpose of the present work is to densify 8YSZ composite by pressureless sintering with MnO₂ additives and to investigate the effect of the additive on the relative density, microstructure and mechanical properties of the composite.

2 Materials and methods

2.1 Sample preparation

A commercially 8YSZ (>99.9 wt %) powder (Wangjing, Hangzhou, China) and an analytical-reagent-grade MnO₂ (Jiayu, Shandong, China) with an average particle size of 3.52 μm and 3.61 μm, respectively were used as raw
materials. Appropriate amounts of powders (The compositions of 8YSZ composite powder were shown in Table 1) were mixed in absolute ethyl alcohol via ball milling for 24 h, using a zirconia jar and high-purity ZrO$_2$ balls, then dried and sieved through 100-mesh screen. After adding 2 wt. % PVA and sieving through a 40-mesh screen, the mixtures were pressed uniaxially to rectangular bars at 60 MPa, followed by cold isostatic pressing at 200 MPa.

### Table 1 The compositions of 8YSZ composite powder, wt. %

| Sample | Composition / wt. % | 8YSZ | MnO$_2$ |
|--------|---------------------|------|---------|
| 1#     | 100.0               | 0.0  |         |
| 2#     | 99.0                | 1.0  |         |
| 3#     | 98.0                | 2.0  |         |
| 4#     | 97.0                | 3.0  |         |
| 5#     | 95.0                | 5.0  |         |

Samples were heated at 5°C/min to 400°C, held for 60 min to detach PVA, and then heated at 5°C/min to the final sintering temperature (1200-1400°C), held for 4 h, finally cooled within the furnace.

### 2.2 Characterization

Crystal-phase identification and phase compositions of the sintered samples were determined by X-ray diffractometry (XRD: G/max-2500, Rigaku Japan) with Ni filtered CuKa radiation. The volume fraction of the monoclinic ($\beta$) phase present in the ceramic matrix was determined using the method of Toraya et al [20], which was shown as the following equation (1). For this purpose, a 0.02° 2$\theta$ step and a count time of 0.5 s per step over the 2$\theta$ range 20-40 which covers the monoclinic ($\beta$) and tetragonal/cubic (t+c) related $\{111\}$ peaks.

$$X_{\beta} = \frac{I_{\beta}(111)+I_{\beta}(\overline{1}1\overline{1})}{I_{\beta}(111)+I_{\beta}(\overline{1}1\overline{1})+I_{\gamma}(111)}$$

(1)

The bulk relative density of the sintered samples was measured by paraffin method (ASTM C373-288 (1999)). Every relative density datum was determined by an average of three similar specimens. The sintered samples were polished and thermal etched at temperatures below 100°C of sintering temperature for 30 min. The microstructures of sintered samples and energy-dispersive spectroscopy (EDS) quantitative analyses were done in a scanning electron microscopy equipped with a microanalyzer GENESIS60S (SEM: Sirion 200, FEI Netherlands). Average grain sizes were determined from the SEM micrographs, using the linear intercept method [21] with at least 300 grains counted for each sample. Rectangular bars for bending strength tests (3 mm×4 mm in cross section and 35-45 mm long) were cut, and three-point bending strength measurements were carried out with an inner span of 30 mm and a crosshead speed of 0.5 mm/s at room temperature using an Instron-1195 Universal Test Machine. At least five specimens were tested per composition. Vickers hardness ($H_v$) measurements (Future Tech., Japan) were made on polished samples using the Vicker’s indentation method. The indentation load was kept constant at 98.1 N and a loading time of 10 s was employed. Six measurements were made for each sample and average values were obtained.

### 3 Results and discussion

#### 3.1 Relative densities of 8YSZ

The relative densities of the samples with different MnO$_2$ additive contents sintered at 1200-1400°C for 4 h are shown in Figure 1.

Fig. 1 shows that the relative density of 8YSZ is significantly improved by the addition of manganese oxide. 8YSZ samples containing ≥3.0 wt. % MnO$_2$ exhibits ~98.6% theoretical density if compared to the undoped ceramic (62.5% theoretical density) when sintered at 1300°C. This is due to the solid solution of MnO$_2$ in ZrO$_2$ crystal (see Fig. 4) may increase lattice defects of the crystal lattice of ZrO$_2$, and then lead to the reduction of diffusion activation energy [19]. Therefore, it may be elaborated that Mn cations substitute the Zr sites, resulting in fast diffusion paths within the single grains during the sintering process. As a result of the faster diffusion paths formed, the process of excessive grain growth is enhanced when the manganese oxide addition is added. Fig. 1 also indicates that, the relative density of 8YSZ almost kept unchanged with the addition content of MnO$_2$ increasing from 3 wt. % to 5 wt. %.

![Graph showing relative density vs. sintering temperature for 8YSZ with different MnO$_2$ contents](image-url)
3.2 Microstructure

Fig. 2 shows a SEM micrograph of polished and thermal etched surface of samples with different MnO₂ content sintered at 1300 °C for 4 h.

Fig. 2 SEM photographs of samples with different MnO₂ content sintered at 1300 °C for 4 h
(a) 8YSZ; (b) 8YSZ+1.0 wt. % MnO₂; (c) 8YSZ+3.0 wt. % MnO₂; (d) 8YSZ+5 wt. % MnO₂

Fig. 2 indicates that, porous structure is observed on the surface of the undoped 8YSZ, and the 8YSZ powder particles is just bonded together, which indicates that the sintering process is not completed. However, after MnO₂ is added into 8YSZ, its surface became compact, and its relative density is enhanced greatly, which is fall-in with Fig.1. When the content of MnO₂ is 1wt%, the average grain size of 8YSZ is very fine, about 0.3 μm, and a very small amount pores are observed at triple grain boundaries (see Fig. 2(b)). With the content of MnO₂ increasing from 1 wt. % to 5wt.%, the average grain size of 8YSZ increases quickly from 0.3μm to 2.5μm, and pores are not observed which may be attributed to the fact that, the rate of 8YSZ grain growth is enhanced when manganese oxide is added [19].

Fig. 3 shows a SEM micrograph of polished and thermal etched surface of samples with 3 wt % MnO₂ sintered at different temperature for 4 h.

Fig. 3 SEM photographs of samples with 3 wt. % MnO₂ sintered at different temperature for 4 h
(a) 1200 °C; (b) 1300 °C; (c) 1400 °C

It can be seen from Fig.3, a small amount pores are observed on the surface of the sample sintered at 1200 °C, however, the surfaces of samples sintered at 1300 °C and 1400 °C are compact, pores and second-phases are not observed. This is due to that, with the increasing of sintering temperature, the diffusion rate of ions is enhanced, which is benefit to increase the densification rate. Fig.3 also indicates that, with the sintering temperature increasing from 1200 °C to 1400 °C, the average grain size of 8YSZ increases gradually from 1.1 μm to 3.2 μm.

The Mn element mapping image and XRD pattern on the polished surface of 8YSZ+3wt%MnO₂ sample sintered at 1300°C for 4h are shown in Fig.4.
Fig. 4 Mn element mapping image and XRD pattern on the polished surface of 8YSZ+3wt. % MnO₂ sample sintered at 1300 °C for 4 h
(a) SEM photography of sample; (b) Element mapping image of Mn; (c) XRD pattern

Fig. 4(a) and (b) indicates that, Mn element is distributed uniformly on the surface of the sample with 3wt. % MnO₂, and second-phase is not observed on the surface, also the diffraction peaks of MnO₂ and second-phase are not found in Fig. 4 (c), which indicates that MnO₂ is successfully doped into the ZrO₂ lattice structure.

The X-ray diffraction patterns (20°-40°) on the polished surface of 8YSZ and 8YSZ+3.0 wt. %MnO₂ samples sintered at 1300 °C for 4 h are given in Fig. 5. And phase compositions of these samples are calculated in Table 2.

Table 2 Monoclinic phase ZrO₂ fraction in bulk samples

| Sample                | Mono. ZrO₂ (%) |
|-----------------------|----------------|
| 8YSZ bulk             | 53.8           |
| 8YSZ+3 wt. % MnO₂     | 12.5           |

The results reveals that, with the additive content increasing from 0 to 3 wt. %, the monoclinic phase ZrO₂ fraction in bulk samples decrease from 53.8 % to 12.5 %, which means that the additions of additive are beneficial to the tetragonal phase stability of these 8YSZ specimens. This is due to the phase transformation of tetragonal phase to monoclinic phase is inhibited by the increased relative density of the samples with higher additive content during the cooling process [22]. The relative high tetragonal content (46.2%) in the sintered body of the undoped ceramic can be attributed to the fact that high sintering temperature (>1300 °C) would have allowed greater tetragonal phase stability to room temperature. Fig. 5 also indicates that, all the main zirconia peaks in the 8YSZ+3.0 wt. %MnO₂ pattern are shifted towards higher angles with respect to the 8YSZ pattern, which may be attributed to the deformation of the crystal lattice of ZrO₂ caused by the solid solution of MnO₂ in ZrO₂ crystal.

3.3 Mechanical properties

The Vicker’s hardness variations with sintering temperatures for the 8YSZ samples with different additive contents are shown in Fig.6.
Fig. 6 Vicker’s Hardness of 8YSZ as function of additive content and sintering temperature

It can be seen from Fig. 6, the Vicker’s hardness of the 8YSZ sample with additive is much higher than that of the sample without additive, and with the additive content increasing, the Vicker’s hardness of sample increase rapidly, and the measured hardness of all the samples reveals a similar trend, i.e. increasing with higher sintering temperatures. In general, the increase in hardness with the increasing of additive content and sintering temperature can be attributed to the increase in bulk density as shown in Fig. 1.

Figure 7 indicates the bending strength of 8YSZ as a function of the sintering temperature and additive content.

![Fig. 7 Bending strength of 8YSZ as function of additive content and sintering temperature](image)

Fig. 7 Bending strength of 8YSZ as function of additive content and sintering temperature

It can be seen from Fig. 7 that, the bending strength of sintered samples increases with the increasing of additive content and sintering temperature when the additive content is below 3 wt. %, which may be attributed to the increasing of relative density. When the additive content is ≥ 3 wt. %, the bending strength of the sample increases gradually with the sintering temperature increasing from 1200 °C to 1300 °C, then decreases with the sintering temperature continually increasing to 1400 °C. This may be due to that, the bending strength is related not only with relative density, but also with the grain size of 8YSZ. Usually, for a ceramic material, the bending strength decreases with the increasing of grain size [15]. Fig. 4 indicates that the average grain size of 8YSZ increases from about 1.4 μm to 3.2 μm with the sintering temperature increasing from 1300 °C to 1400 °C, however, the relative density keeps almost unchanged, which results in the decreasing of relative density. For the same reason, the bending strength of the sample with 3 wt. % additives is higher than that of the sample with 5 wt. % additives.

4 Conclusions

(1) The addition of manganese oxide is beneficial in aiding sintering of 8YSZ ceramics, particularly when sintered at low temperature, below 1300 °C. The relative density of sample increases with the increasing of additive content and sintering temperature.
(2) Additions of MnO₂ are beneficial in achieving high tetragonal phase retention and the grain size of sample increases with the increasing of additive content and sintering temperature.
(3) The hardness and bending strength of MnO₂ doped samples are generally much higher than that of the undoped ceramics, and the hardness increase with the increasing of sintering temperature and additive content.
(4) When the addition content of MnO₂ is below 3.0 wt %, the bending strength increases with the increasing of addition content and sintering temperature.

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