JOURNALOF

Ceramic Processing Research

Inter-granular phase formation and flexural strength of MgO partially stabilized zirconia by Al₂O₃ additions

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Phase transformation and inter-granular phase formation of 9 mol% MgO partially stabilized zirconia (Mg-PSZ) according to Al_2O_3 addition were investigated in terms of crystallography and morphology, and its flexural strength was measured. Sintered bulk specimens of 9 mol% Mg-PSZ ball-milled with Al_2O_3 (1, 5, 10 mol%) were evaluated by X-ray diffraction, transmission electron microscopy and EDS. Monoclinic phase in Mg-PSZ, which has a larger lattice than that of cubic and tetragonal phases, increased as a function of Al_2O_3 addition. The apparent density of Mg-PSZ was decreased with increasing Al_2O_3 addition, and flexural strength was also exibited the lowest value with 10 mol% Al_2O_3 addition. Mg-rich phase, forsterite (Mg_2SiO_4), and spinel (MgAl_2O_4) were observed along grain boundary of Mg-PSZ with Al_2O_3 additon by TEM-EDS. It was considered that destabilization of Mg-PSZ by Al_2O_3 addition led to decrease the apparent density, and countinuous intergranular phase formation caused the decrease of flexural strength.

Key word: Magnesia partially stabilized zirconia (Mg-PSZ), Al₂O₃ addition, Destabilization, Flexural strength, Inter-granular phase.

Introduction

Zirconia-based solid electrolytes have been used in solid oxide fuel cells (SOFCs), oxygen sensors, and oxygen pumps, because they exhibit outstanding ionic conductivity, thermal stability, and mechanical strength [1, 2]. Zirconia exists in three crystallographic phases, which are monoclinic under 1170 °C, tetragonal between 1170 °C and 2370 °C, and cubic phase from 2370 °C to melting point [3]. It is possible to stabilize the cubic phase at room temperature by doping with an oxide, such as Y_2O_3 , CaO, MgO, and etc. [4].

During the sintering of zirconia-based solid electrolyte, SiO_2 , an impurity of zirconia, forms a continuous siliceous phase on the grain boundary, and the siliceous film impedes the transfer of oxygen ions. [5, 6]. Various additives, such as Fe_2O_3 [7], Bi_2O [7], TiO_2 [8], Al_2O_3 [9] have been investigated for release the harmful effect of the siliceous phase on the grain boundary. The siliceous phase was formed around the additive, and it is known as scavenging effect [9-11]. Al_2O_3 has been reported as one of the most effective additives in Y_2O_3 -ZrO₂ and CaO-ZrO₂ systems [12, 13]. The Al_2O_3 addition also affects mechanical properties of the Y_2O_3 -ZrO₂, such as fracture strength and toughness [14, 15].

Magnesia partially-stabilized zirconia (Mg-PSZ) is an

appropriate material for high temperature applications, such as an oxygen-permeating membrane for removing oxygen from molten steel, due to its better mechanical and thermal properties, as compared to yttria-stabilized zirconia (YSZ) [16, 17]. In the previous study, however, we proved that Al was located with Mg rather than Si in Mg-PSZ and it caused increase of grain boundary resistance [18]. Therefore, it is necessary to understand the mechanisms of phase formation and flexural strength by Al₂O₃ addition in Mg-PSZ.

The current study has examined the flexural strength of 9 mol% Mg-PSZ according to Al_2O_3 addition (1, 5, and 10 mol%), and inter-granular phase formation in the Mg-PSZ by Al_2O_3 was investigated by crystallographical and microstructural analyses.

Experimental Procedure

9 mol% MgO doped zirconia powder with 0.03 wt.% impurity concentration of SiO₂ (UCM Advanced Ceramics GmbH, HQB 0150) was used to produce the Mg-PSZ. The addition of alumina (Junsei Chemical Co. Ltd.) in the Mg-PSZ powder was prepared by ballmilling with zirconia balls for 24 h. Table 1 shows the composition and designation for the evaluated specimens. The powders were pressed using a cylindrical (20 mm in diameter) and a bar type (length 60 mm and width 7 mm) mold under a uniaxial pressure of 20 MPa. The green bodies were sintered at 1600 °C for 6 h in air.

Phase transformation of the sintered powders was analyzed by X-ray diffraction (XRD, Rigaku, Ultima-

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	Composition			
Denotation	Raw material	Al ₂ O ₃ addition (mol%)		
Mg-PSZ		_		
Mg-PSZ_1A1	$0 \approx 10/M_{\odot}$ DS7	1		
Mg-PSZ_5A1	9 mol% Mg-PSZ	5		
Mg-PSZ_10A1		10		

Table 1. Designation of Mg-PSZ specimens with Al₂O₃ addition.

IV) over a 2θ range of $20-90^{\circ}$ with a scan speed of $1^{\circ}/$ min and a scan step of $0.02^{\circ}/2\theta$ at room temperature. The background and XRD peak shape were fitted with a fifth-degree polynomial and a pseudo-Voight function. The microstructure of the specimens was observed with a field emission scanning electron microscope (FE-SEM, Hitachi, S-4800). The mechanical properties were evaluated by measuring an apparent density with the Archimedes method and the flexural strength with a 3-point flexural test. The specimens for microstructural analyses were prepared by focused ion beams (FIB, FEI, Quanta 3D FEG). The formation of second phase on grain boundary was observed, using transmission electron microscopy (TEM, JEOL, JEM-2100F).

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the sintered Mg-PSZ powder with according to Al_2O_3 addition. All specimens exhibit a mixture of cubic, tetragonal, and monoclinic phases, which is in good agreement with the 9 mol% Mg-PSZ [19]. The peaks at 28.2 ° and 31.4 ° indicate the monoclinic phase, and the peak at 30.4 ° corresponds to the cubic phase. The peak intensities for the cubic and tetragonal phases decreased, and the monoclinic phase increased due to destabilization of Mg-PSZ with an increase in Al_2O_3 addition. The volume fraction of the monoclinic phase in Mg-PSZ, calculated by the method of Potter and Heuer [20],



Fig. 1. X-ray diffraction patterns and volume fraction of monoclinic phase (*Vm*) in Mg-PSZ according to Al₂O₃ addition.



Fig. 2. Surface of Mg-PSZ with different Al2O3 additions: (a) Mg-PSZ, (b) Mg-PSZ_5Al, and (c) Mg-PSZ_10Al.

increased from 0.0799 (Mg-PSZ) to 0.9872 (Mg-PSZ_10Al) with Al₂O₃ additions. The cubic phase undergoes a decomposition reaction with the addition of Al₂O₃ [18]. The peak at 24 ° assigned to the monoclinic phase and the peaks for the spinel phase were observed in the specimens with 5 and 10 mol% Al₂O₃ additions. The results indicate that the reaction, between the stabilizer (Mg in Mg-PSZ) and the Al₂O₃, causes a destabilization of Mg-PSZ.

Figure 2 shows the surface morphologies of the sintered Mg-PSZ with different Al_2O_3 additions after sintering at 1600 °C for 6 h. Two types of grains clearly presented on the surface of the Mg-PSZ (see Fig. 2(a)). The fine grains (indicated by circles in Fig. 2(a)) are the monoclinic phase, and the relatively larger grains are the cubic phase [19]. The monoclinic phase increased with increasing Al_2O_3 addition, as shown in Fig. 2(b) and (c). The results of this observation are consistent with the crystal structures of the specimens,



Fig. 3. (a) Apparent density and (b) flexural strength of Mg-PSZ according to Al_2O_3 addition.

as shown in Fig. 1, and indicates that the Al_2O_3 addition acts as a destabilizer, which led to a phase transformation to the monoclinic, and the phases formed at grain boundary.

Figure 3 shows the apparent density and flexural strength measurements for the Mg-PSZ according to Al_2O_3 addition. The density tended to decrease with increasing in Al_2O_3 , and the density of the specimen with 10 mol% Al_2O_3 addition drastically decreased from 5.7348 (Mg-PSZ) to 5.077 g/m³ (Mg-PSZ_10Al). This result indicates that the destabilization of Mg-PSZ by addition of Al_2O_3 causes an increase in the monoclinic phase, which has a larger volume (0.1403 nm³) than the cubic phase (0.1305 nm³) and the tetragonal phase



Fig. 5. Bright-field TEM images of (a) Mg-PSZ and (b) Mg-PSZ_1Al.

 (0.1328 nm^3) [20]. The flexural strength of Mg-PSZ was 528.65 MPa, and the strength decreased as a function of Al₂O₃ addition, and the specimen with 10 mol% Al₂O₃ showed the lowest value at 22.59 MPa.

In order to research the degradation mechanism of flexural strength, additional microstructural analyses were conducted to investigate phase formation on the grain boundary of Mg-PSZ by Al₂O₃ addition. Figure 4 shows surface of FIB-milled region for TEM analysis



Fig. 4. FIB-milled region for TEM specimen preparation and SEM-EDS profiles of Mg-PSZ_1Al.



Fig. 6. Inter-granular phase and SAD patterns on the grain boundary of the Mg-PSZ_1Al.

and SEM-EDS data on grain boundary of Mg-PSZ_1Al. Point A marked on grain boundary without a second phase, and point B indicates the grain boundary with of Mg-PSZ_1Al. In order to investigate the phase formation on the grain boundary, the specimen for TEM analysis was included the Al-containing spot B comparing with spot A.

Figure 5 shows TEM observations of Mg-PSZ and Mg-PSZ_1Al. Discontinuous phase was found on grain boundary of Mg-PSZ (see Fig. 5(a)). In contrast, 1 mol% Al₂O₃ addition into Mg-PSZ led to continuous second phase formation along the grain boundary. Strength loss of ceramics is well known that it is attributed to the formation of a continuous second phase formation at grain boundaries during fabrication [21]. Therefore, the phase formation along the grain boundary by Al₂O₃ addition deteriorated flexural strength of Mg-PSZ.

Figure 6 shows TEM SAD patterns of at point A marked on internal grain, and points B, C, and D indicate second phases on the grain boundary of Mg-PSZ_1Al. SAD patterns on B, C, and D presented multi phases, unlike A showed single fluorite phase. Table 2 shows TEM-EDS profiles and B, C, and D were identified as Mg-rich phase, spinel (MgAl₂O₄), and forsterite (MgSiO₄), respectively. These results indicate that the addition of Al₂O₃ contributes to the reaction with Mg in Mg-PSZ, rather than scavenging the siliceous phase. Therefore, the reaction led to destabilization and the formation of inter-granular phases along grain boundary of Mg-PSZ.

Conclusions

The effect of Al₂O₃ content on 9 mol% Mg-PSZ was investigated in terms of phase transformation and intergranular phase formation. The cubic phase of Mg-PSZ was transferred to monoclinic phase with increase in Al₂O₃ addition and the cubic-to-monoclinic transformation decrease apparent density. Flexural strength of Mg-PSZ also decreased as a function of Al₂O₃ addition. Second phases formation by Al₂O₃ were observed along the grain boundary of Mg-PSZ 1Al. The second phase

Table 2. TEM-EDS point profiles on the grain boundary of the Mg-PSZ_1Al.

А	Element	Weight%	Atomic%	В	Element	Weight%	Atomic%
	О	6.86	28.84		0	12.63	31.25
	Mg	0.46	1.28		Mg	25.32	41.21
	Si	0.92	2.20		Si	0.65	0.91
	Zr	91.76	67.68		Zr	61.40	26.63
	Totals	100.00			Totals	100.00	
С	Element	Weight%	Atomic%	D	Element	Weight%	Atomic%
	О	13.40	36.51		0	7.98	24.78
	Mg	5.51	9.52		Mg	1.59	6.61
	Al	10.87	18.81		Al	0.14	0.34
	Si	1.03	1.62		Si	1.40	6.12
	Zr	69.19	33.53		Zr	88.89	62.15
	Totals	100.00			Totals	100.00	

formations were evaluated by SAD patterns and identified by TEM-EDS analyses as being Mg-rich phase, spinel, and forsterite. Therefore, the mechanism of decrease in the density of Mg-PSZ with Al₂O₃ additions is considered to be the destabilization of Mg-PSZ, caused by the reaction between Al₂O₃ and Mg in Mg-PSZ. The reaction contributes to inter-granular phase formation, which led to a deteriorated the flexural strength.

Acknowledgments

This work was supported by the Financial Supporting Project of Long-term Overseas Dispatch of PNU's Tenure-track Faculty, 2013. We are also especially appreciative to Ms. Mary Van Tyne for her language editing of the manuscript.

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