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Effects of manganese oxide addition and reductive atmosphere annealing on the phase stability and microstructure of yttria stabilized zirconia

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Abstract

The effects of Mn_3O_4 addition and reductive atmosphere (N_2:H_2 = 97:3) annealing on the microstructure and phase stability of yttria stabilized zirconia (YSZ) ceramics during sintering at 1500 °C for 3 h in air and subsequent annealing in a reductive atmosphere were investigated. Mn_3O_4 added 6 mol% YSZ (6YSZ) and 10 mol% YSZ (10YSZ) ceramics were prepared via the conventional solid-state reaction processes. The X-ray diffraction results showed that a single cubic phase of ZrO_2 was obtained in 1 mol% Mn_3O_4 added 6YSZ ceramic at a sintering temperature of 1500 °C for 3 h. A trace amount of monoclinic ZrO_2 phases were observed for 1 mol% Mn_3O_4 added 6YSZ ceramics after annealing at 1300 °C for 60 cycles in a reductive atmosphere by transmission electron microscopy. Furthermore, a single cubic ZrO_2 phase existed stably as Mn_3O_4 added 10YSZ ceramics was annealed at 1300 °C for 60 cycles in reductive atmosphere.

Keywords: Manganese; Yttria stabilized zirconia (YSZ); Aging test; Superlattice; Oxygen partial pressures

1. Introduction

In the recent years, yttria stabilized zirconia (YSZ) applied to solid oxide fuel cells, thermal barrier coatings, reverse flow reactors, and advanced structural ceramics has received considerable research attention because of their excellent oxygen-ion conductor, high fracture toughness, and low thermal conductivity.[1–6] Pure ZrO_2 has cubic fluorite structure upon cooling from its melting point (2680 °C), and then transforms from tetragonal form at 2370 °C to monoclinic form at 1170 °C.[7] In view of its applications, the metastable cubic phase is the most suitable. One of the major challenges is therefore to control and tune the crystallographic phase. The introduction of cations with valence less than 4, such as Y^{3+}, Ca^{2+}, and Mg^{2+}, creates a high concentration of oxygen vacancies that can stabilize the high temperature structure phases to room temperature. According to the two component phase diagram (ZrO_2-$YO_{1.5}$),[8,9] ZrO_2 can be stabilized in cubic fluorite structure at lower temperatures, with an Y_2O_3 content of approximately 8 mol% at 1300–1400 °C. However, tetragonal precipitates were observed in a cubic matrix at Y_2O_3 contents between 5 mol% and 8 mol%.

Manganese ions can dissolve into YSZ, with a solubility limit between 5 mol% at 1000 °C and 15 mol% at 1500 °C.[10] Appel et al. reported that a single cubic structure could be retained for 7.5 mol% YSZ with 2 mol% or more Mn at 1400 °C.[11] On the other hand, the valence state of Mn may change with the oxygen partial pressure.[12] Kawada et al.[10] found that all Mn^{3+} in stabilized zirconia could be reduced to Mn^{2+} at oxygen partial pressure lower than 10^{-10} Pa. Therefore, oxygen vacancies were generated when Mn^{2+} ions were substituted into the Zr^{4+} site at low oxygen partial pressure. Moreover, the oxygen vacancies are reported to be one of the most important effects which can make high symmetry phase retain to room temperature.[8]

Multilayer ceramic capacitors (MLCCs) are placed on ZrO_2 ceramic plates that supported MLCC chips for sintering. However, using partial stabilized zirconia ceramic plates for sintering may cause changes in the temperature dependence of permittivity and dielectric loss to reduce reliability in the fabrication of MLCCs. In the recent years, low-cost metals were used for the inner electrodes of MLCCs such as Ni and Cu. Consequently, the MLCCs must be sintered in a reductive atmosphere.[13,14] In this study, the phase stability and microstructure of YSZ ceramics with Mn_3O_4 addition levels ranging from 0 mol% to

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1.5 mol% were investigated. Furthermore, the effect of reductive atmosphere annealing on the phase stability of Mn added YSZ ceramics was thoroughly studied using the state-of-the-art analytical instruments, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and field-emission transmission electron microscopy (TEM).

2. Experimental procedure

A conventional solid-state reaction method was used to prepare the present 6 mol% and 10 mol% of Y_2O_3 stabilized ZrO_2 samples (6YSZ and 10YSZ) from commercial powders of ZrO_2 (KCM Corporation, Japan, >99.9%) and Y_2O_3 (Chem-Service Inc., USA, >99.9%). The ZrO_2 and Y_2O_3 powders were mixed with deionized water and Ø 2-mm zirconia beads in a ball-milling bottle for 24 h (ball-to-water-to-powder ratio is 12:2:1, rotation rate: 62 rpm). The mixture was dried at 125 °C, calcined at 1400 °C for 6 h in air, and then crushed into powder. Different amounts of Mn_3O_4 (0.1, 0.2, 0.3, 0.4, 0.5, 1.0, and 1.5 mol%) were mixed with the 6YSZ and 10YSZ powders using the same procedure. These powders were mixed with the binder (polyvinyl alcohol) additive, and then pressed into disk-shaped specimens. The pellets were sintered at a temperature of 1500 °C for 3 h in air, with a heating rate of 3 °C/min.

The thermal aging test was conducted to anneal the samples, including 6YSZ and 10YSZ ceramics, with different Mn_3O_4 additions. The samples were annealed at 1300 °C for 2 h, with a heating rate of 5 °C/min, in flowing dry gas (N_2:H_2 = 97:3), and with subsequent furnace cooling in a tube furnace, which is termed a cycle for the thermal aging test. The oxygen partial pressures of dry gas mix was about 1×10^{-10} Pa.

The crystallinity of the sintered samples were analyzed by high-resolution XRD (Bruker D8D, Germany), with Cu-Kα radiation for 2θ from 20° to 80° at a scan speed of $2^\circ\ \mathrm{min}^{-1}$. The DIFFRAC plus TOPAS version 3.0 program was used to determine the lattice parameters. Interior microstructure observation of the sintered ceramics was conducted by SEM (JEOL JEL-6400, Tokyo, Japan). Average grain size measurements were conducted using a linear intercept method complying with the British Standard BS EN 623-3:2001 where the number of grains analyzed per samples was about 400. The interior microstructure of the sintered ceramics was investigated by filed-emission TEM (JEOL JEM-2100F, Tokyo, Japan) at an accelerating voltage of 200 kV. The specimens for TEM observations were prepared by slicing, mechanical grinding, and ion milling at 4.0 kV. The bulk density of the sintered pellets was measured using the Archimedes method and the number of 10 samples was used for averaging the values.

3. Results and discussion

3.1. Mn_3O_4 added 6YSZ ceramics

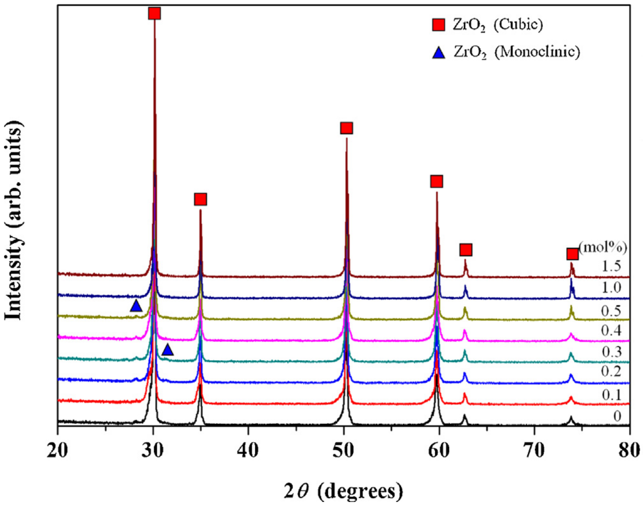

Fig. 1. XRD spectra of the 6YSZ ceramics with different amounts of Mn_3O_4 addition sintered at 1500 °C for 3 h.

The effects of Mn_3O_4 addition on the microstructure characteristics and phase evolution of 6YSZ ceramics were evaluated. The crystalline phase of the seven Mn_3O_4-containing samples was measured by XRD. Fig. 1 shows the XRD spectra of the 6YSZ ceramics with 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, and 1.5 mol% Mn_3O_4 addition sintered at 1500 °C for 3 h. A change in crystal phase was observed with the increase of Mn_3O_4 content. The undoped 6YSZ ceramic has cubic and monoclinic phases (c-ZrO_2 and m-ZrO_2). The intensity of the peaks for monoclinic phases decreased significantly as the Mn_3O_4 content increased to 0.5 mol%, and then disappeared when Mn_3O_4 content reached 1.0 mol% and above, illustrating that Mn_3O_4 addition is an effective approach to stabilize ZrO_2 in its cubic phase at room temperature. The oxidation state of Mn in solid solution in zirconia is a mixture of Mn^{2+} and Mn^{3+} when Mn added ZrO_2 ceramics was sintered in air.[11] Two double ionized oxygen vacancies were formed simultaneously when Mn ions were substituted into the Zr site, i.e.,

$$Mn_3O_4 \xrightarrow{ZrO_2} 2Mn'_{Zr} + Mn''_{Zr} + 2\ddot{V}_O + 4O_O^X \qquad (1)$$

where $\ddot{V}_O$, Mn'_{Zr}, and Mn''_{Zr} are the oxygen vacancy, Mn^{3+}, and Mn^{2+}, respectively. In other words, an increasing Mn-content in YSZ results in an increasing concentration of oxide vacancies. The oxygen vacancies have been reported to be the one of most important effects which can make the cubic phase retain to temperature. Cubic to monoclinic phase transformation is driven by the decrease of the oxygen vacancy quantity and modification of the valence state of Mn ions.[15]

Fig. 2 presents the SEM micrographs showing different surface morphologies of the 6YSZ ceramics with 0, 0.1, 0.3, 0.5, 1, and 1.5 mol% Mn_3O_4 addition sintered at 1500 °C for 3 h. The microstructures tend to be closely correlated with the Mn_3O_4 content. We found that for the YSZ with lower Mn_3O_4 content, the large grains are found accompanied by small crystals surrounding along the grain boundaries; further increasing the Mn_3O_4 content, typical equiaxed grains are obtained and a good particle packing is reached. According to the XRD analysis, it is obvious that the grain size is small for the two-phase structure, whereas the grains for the single cubic structure grow up very fast. Several investigations have found that the grain growth of single-phase structure is faster than in two-phase structure and